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THE
IRON AND STEEL INSTITUTE
CARNEGIE SCHOLARSHIP
MEMOIRS

VOL. IV.

EDITED BY
GEORGE C. LLOYD
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Printed by BALLANTYNE, HANSON & CO.
At the Ballantyne Press, Edinburgh

DETAILED CONTENTS.

	PAGE
THE PRESERVATION OF IRON BY MEANS OF PAINT. By J. NEWTON FRIEND, D.Sc., Ph.D. (Darlington)	1
THE FIELD TESTS.	
I. The nature of the liquid vehicle	4
1. The chemical permanence of linseed oil	4
2. The porosity of oil films	10
3. Electrical insulation	12
II. The physical condition of the pigment	16
1. The size of the pigmentary particles	17
2. The porosity of the pigmentary particles	21
3. The colour of the pigment	21
4. The solubility of the pigment	22
5. The galvanic activity of the pigment	22
6. The hygroscopicity of the pigment	23
III. The chemical condition of the pigment	24
IV. The condition of the iron surface to be painted	24
V. The method of application of the paint	25
APPENDIX	26
THE CONSTITUTION OF THE SULPHIDE ENCLOSURES IN IRON AND STEEL AND THE DESULPHURISATION PROCESS. By G. RÖHL, Dipl.Ing. (Freiberg, Saxony)	
28	
Production of the melted components in a chemically pure state	34
The iron	34
Ferrous sulphide	35
Manganese sulphide	36
Reactions for the recognition of sulphide enclosures	37
Reactions for distinguishing between ferrous sulphide and manganese sulphide	40
Examination of the system $\text{FeS} - \text{MnS}$	49
The thermal diagram and the micrographic results	52
The influence of manganese sulphide on the binary eutectic $\text{Fe} - \text{FeS}$	56
Microscopical results	61
Sulphides of different manganising stage in the large iron-excess	65
Influence of the carbon content on the sulphide enclosures	69
Influence on the sulphide enclosures of a manganese content in the melt	71
The importance of manganese for the desulphurisation	75

	PAGE
THE INTERCRYSTALLINE FRACTURE OF IRON AND STEEL. By J. C. W. HUMFREY, M.A., M.Sc., M.Eng. of the National Physical Laboratory	80
Intercrystalline brittleness in electrolytic iron	82
Pure reduced iron	84
Transformer sheet	85
Experiments on annealing Swedish iron <i>in vacuo</i>	87
Experiments on annealing in nitrogen	94
Reheating and quenching experiments	95
Conclusions	96
APPENDIX	102
Apparatus employed in the experimental work	102
Furnace for prolonged annealing <i>in vacuo</i>	102
Furnace for melting iron <i>in vacuo</i>	103
Furnace used for reheating and quenching experiments	105
THE PRODUCTION OF STEELS AND FERRO-ALLOYS DIRECTLY FROM ORE IN THE ELECTRIC FURNACE. By ROBERT M. KEENEY, E.Met. (Colorado)	108
Introduction	108
Part I.—Historical data	108
Part II.—Research upon the production of steels and ferro-alloys directly from ores in the electric furnace	108
PART I.	
Historical data	110
The production of steel directly from ore	110
The production of steel directly from iron ore in the electric furnace	111
Experiments of Stassano	112
Investigations of J. W. Evans	115
Investigations of W. G. Brown and F. E. Lathe	116
Experiments of "La Neo-Metallurgie"	117
The application of the Lash process to the electric furnace	120
Previous research of the author	121
The production of alloy steels directly from ores in the electric furnace	123
Investigations of Dittus and Bowman on the direct production of molybdenum steel in the electric furnace	123
Previous research of the author on the production of tungsten steel directly from ore in the electric furnace	125
The production of ferro-alloys directly from ore in the electric furnace	126
Ferro-chromium	127
Investigations of Neumann on the direct production of ferro- chromium	129
Experiments of Moissan	129

	PAGE
Ferro-molybdenum	130
Experiments of Guichard	130
Experiments of Lehner	130
Experiments of Neumann	131
Ferro-tungsten	131
Decarburisation of ferro-tungsten	132
Experiments of Stassano	133
PART II.	
Research upon the production of steels and ferro-alloys directly from ores in the electric furnace	134
Experimental furnaces	134
Apparatus and instruments	140
The production of steel directly from ore in the electric furnace	142
Theoretical considerations	142
I. Consumption of carbon	142
II. Amount of slag	144
III. Amount of gas evolved	144
IV. Heat of combustion of carbon	144
V. Heat balance	145
VI. Heat balance, using limestone instead of lime	145
Experiments	146
Preliminary experiments	146
Calculations	146
Series I.: Several variables	150
Series II.: Variation of coke in the charge	150
Series III.: Variation of limestone in the charge	153
Series IV.: Variation of fluorspar in the charge	154
Series V.: Continuous experiment No. 23	156
Discussion of results	157
Products	157
Regulation of carbon	158
Silicon in the steel	161
Phosphorus in the steel	161
Sulphur in the steel	163
Physical and metallographic properties	163
Slags	164
Loss of iron in the slag	164
Operation of the furnace	165
Electrodes	166
Steel produced	167
Energy consumption	167
A continuous process for the production of steel directly from ore in the electric furnace	167
Cost of production of steel directly from ore	169
Conclusions	169

	PAGE
The production of chromium steel directly from ore in the electric furnace	170
Experiments	170
Conclusions	172
The production of molybdenum steel directly from ore in the electric furnace	173
Experiments	173
Conclusions	175
The production of tungsten steel directly from ore in the electric furnace	175
Experiments	175
Conclusions	177
The production of ferro-chromium directly from chromite in the electric furnace	177
Experiments	177
Conclusions	180
The production of ferro-molybdenum directly from ore in the electric furnace	180
Experiments	180
Conclusions	181
The production of ferro-tungsten directly from ore in the electric furnace	181
Experiments	181
Conclusion	183
BIBLIOGRAPHY	183

LIST OF PLATES.

Plate	I. Photograph illustrating Dr. Friend's Report . . .	<i>To face page 24</i>
„	II. to VI. Photomicrographs illustrating Mr. Röhl's Report „	72
„	VII. „ XIV. „ „ Mr. Humfrey's Report „	104
„	XV. „ XX. „ „ Mr. Keeney's Report „	184

THE PRESERVATION OF IRON BY MEANS OF PAINT.¹

By J. NEWTON FRIEND, D.Sc., Ph.D. (DARLINGTON).

IN a recent communication² the results were given of a few preliminary experiments carried out with the object of determining the relative values of various liquid vehicles capable of being employed in the manufacture of paint for the protection of iron and steel. Through the kindness of the Carnegie Scholarship Committee, who awarded the author a further grant in May 1911, it has been possible for him to extend these experiments during the past year, and to institute a series of "field" tests with large iron plates exposed in the open air. These when completed will, it is hoped, yield results of considerable value to the engineer and painter.

Inasmuch as some of these tests require several years for their completion and fresh ones are being continually set up as observation proves them to be desirable, this report may be regarded as an introduction to further reports which the author hopes to present as years roll by.

THE FIELD TESTS.

Two types of field test are employed, namely, "air" and "water." The air tests consist in exposing sheets of iron, of the dimensions shown in Fig. 1, to the prolonged action of the atmosphere, and observing the condition of their painted (or unpainted) surfaces from time to time. The actual quantitative determination of their corrosion is only made at the conclusion of the test by scraping off the paint film and any adhering rust, and finding the resulting loss in weight.

¹ Received February 6, 1912.

² *Carnegie Scholarship Memoirs*, 1911, vol. iii. p. 1.

The plates were all cut to one size, and only those cut from one and the same large sheet of metal were regarded as capable of yielding comparable results.

In order to remove the scale, the plates were pickled in dilute sulphuric acid for several hours, then washed in dilute caustic soda, and finally scrubbed under flowing water. On drying at 100°C. , the plates were bright and smooth, and inasmuch as they were all treated in the same manner, the results obtained with them should be strictly comparable.

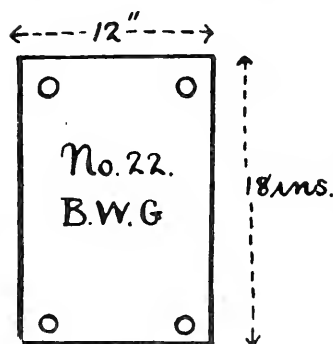


FIG. 1.—Iron Plate used in Air Tests.

After weighing and painting, the plates were suspended to a specially constructed wooden fence by means of four strips of iron bent in the form of hooks, as shown in Plate I. As the plates were separated from one another by an air space of some 4 to 6 inches, and the iron hooks were likewise some distance apart, the possibility of galvanic action occurring between any two adjacent plates was thereby reduced to a minimum.

The water tests are carried out in tanks made of canary wood 1 inch thick. Two such tanks have been made, one measuring 34 inches long, 12 inches broad, and 12 inches deep, internally; the other being twice as long, namely, 70 inches, but with the same remaining dimensions. The troughs were coated internally with molten paraffin wax, in order to prevent rotting of the wood and solution in the water of any soluble substances likely to affect the experiments. Externally the troughs were coated with boiled linseed oil and exposed to the open air. The iron plates used were of the shape and dimension shown in Fig. 2, being made of similar metal to the plates described above in connection with the air tests.

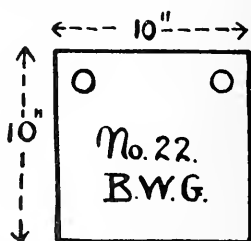


FIG. 2.—Iron Plate [used] in Water Tank Experiments.

In order to prevent galvanic action, they were each suspended by two glass hooks from a glass rod lying across the tank, as shown in Fig. 3.

By keeping the plates at distances of 4 inches apart, sufficient space was left between them for the air to percolate freely through the water. As has recently been shown,¹ it is not advisable to have the plates too close to one another, as the resulting corrosion is then irregular and less than it would otherwise be.

Both tanks were filled with ordinary tap water and exposed freely in a yard to rain, wind, and frost, any water lost through leakage or evaporation being replenished as occasion required.

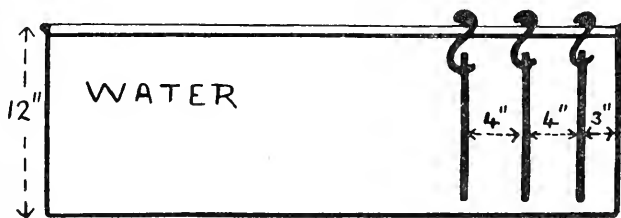


FIG. 3.—Arrangement of Iron Plates in the Water Tank.

These details have been given fully, both to enable others to repeat or extend these experiments if they so desire, and to illustrate what care must be taken to ensure absolute uniformity of treatment throughout any series of experiments, if comparable results are to be obtained. Much otherwise excellent work in this field has been rendered practically valueless owing to lack of details of the experimental manipulation.

Five lines of research suggested themselves as worthy of special study, namely:—

1. The nature of the liquid vehicle.
2. The physical condition of the pigment.
3. The chemical nature of the pigment.
4. The condition of the iron surface to be painted.
5. The method of application of the paint.

We shall proceed to deal with each of these points in such detail as the experiments permit.

¹ Friend, West, and Bentley, *Journal of the Iron and Steel Institute*, 1912, No. 1.

I.—THE NATURE OF THE LIQUID VEHICLE.

A little consideration will show that a liquid vehicle suitable for the protection of ironwork should excel in the following particulars:—

1. Chemical permanence.
2. Imperviousness towards air and moisture.
3. Electrical insulation.
4. Chemical inertness towards iron.
5. Resistance towards physical damage.
6. Elasticity.
7. Setting or drying power.

In the present research pure boiled linseed oil has been employed, of specific gravity 0.955, and saponification number (potash) 18. It has already been shown that this oil, when pure and not contaminated with traces of free acid, exerts a negligibly small corrosive action upon iron. It now remains, therefore, for us to study the other essential properties of the oil, and in the present section we shall confine ourselves to the first three.

1. *The Chemical Permanence of Linseed Oil.*

The drying oils owe their valuable property of setting on exposure to the air to their power of combining with free oxygen to yield tough, solid elastic bodies, to which, in the case of linseed oil, the generic name of linoxyn is usually applied. This change is accompanied by an increase in weight, as indicated by the rise of the curve ABC from A to B, in Fig. 4. Now if the chemical action stopped at this point, the paint film produced would be delightfully permanent, and its useful life greatly prolonged. But, unfortunately, such is not the case, for still more oxygen is now absorbed, and the linoxyn begins to break down into water, carbon dioxide, formaldehyde, &c., as shown by the drop in the curve from B to C. As a matter of fact, the oil has set to a solid mass at about the stage represented by the point D, and the linoxyn has already begun to disintegrate here, but the loss in weight produced thereby is less than the gain in weight

caused by the absorption of oxygen; hence the curve continues to rise. At B the two factors exactly balance, and from B to C the loss is greater than the gain, but the process proceeds with increasing slowness. When, however, the fall from B to C is practically equal to the gain from A to B, the film begins to disintegrate and peel. Such old films are a source of serious danger to ironwork, inasmuch as they not only fail to protect the metal, but actually stimulate corrosion by reason of the induced galvanic activity, the metal serving as anode, and the film as cathode, the latter hiding

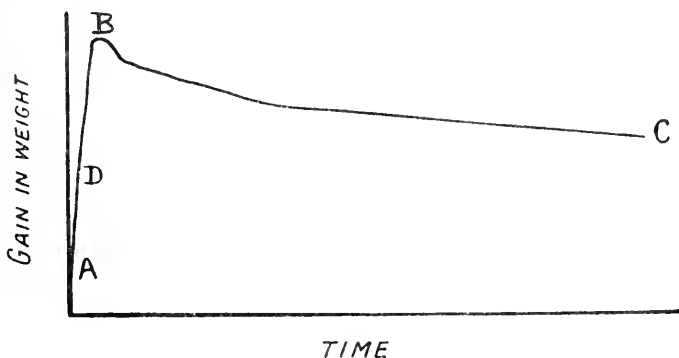


FIG. 4.—Showing the alteration in weight experienced by a film of linseed oil exposed to air.

to a large extent the damage it is causing, and thus rendering it all the more insidious.¹

For this reason, it is desirable to scrape off the paint when once it has begun to crack, and to apply a fresh coating. All the drying oils are open to this objection, and the problem resolves itself into a discovery either of a fresh type of liquid vehicle, or else of a means of preventing the oxidation of the linoxyn, if a really permanent paint is to be produced. Numerous attempts have been made to utilise other liquid vehicles, such as solutions of nitrated cellulose in organic solvents, *e.g.* amyl acetate; and very few researches appear to have been directed towards the possibility of rendering linoxyn permanent. The present author believes, however,

¹ W. H. Walker and J. Lewis, *Industrial and Engineering Chemistry*, 1909, I. No. 2.

that the latter field bids fair to yield a rich harvest of results, and this belief apparently receives justification from the observations now to be described.

Since paraffin wax is a remarkably inert and impervious material, it seemed probable that by dissolving some of it in linseed oil, the latter would be rendered less porous to air and oxygen; and hence, when once oxidised in a paint film, the linoxyn should remain very permanent, owing to the difficulty with which oxygen could gain access to it to effect its disintegration. This supposition was put to the test in the following manner:—

Five glass flasks were placed in a hot water bath at about 95°C ., and equal quantities of pure boiled linseed oil added to each. When the oil had attained to the temperature of the bath, carefully weighed shavings of paraffin wax (M.P. approximately 50°C .) were added to four of the flasks. The latter were now closed with indiarubber bungs and gently shaken until the wax had dissolved and thoroughly homogeneous liquids resulted. After about 40 minutes the flasks were removed from the bath, labelled, and allowed to cool slowly with frequent agitation. Flask A contained pure boiled oil only; flask B, oil + 0.1 per cent. (by weight) of paraffin wax; flask C, oil + 0.3 per cent. wax; flask D, oil + 0.5 per cent. wax; flask E, oil + 1.0 per cent. wax.

Small quantities of these oils were now smeared on to a series of glass slides, measuring $3\frac{1}{4} \times 4\frac{1}{4}$ inches in area, and exposed to the air, being protected as far as possible from dust by a large sheet of glass, one side of which was "ground" in order to minimise any dangers of unequal illumination. The plates were weighed at intervals, with the results given in Table I. and shown graphically in Fig. 5. Inasmuch as the oil films were very thin, these results may be taken as representative of the changes going on during the setting and subsequent exposure of corresponding paint films. It was not found practicable to employ higher percentages of paraffin wax, as the oil was thereby rendered too viscous or even solid, so that, unless thinned down with turpentine or raised to about 80 to 100°C . to effect its liquefaction, the mixture could not be used for painting purposes.

TABLE I.—*The Alteration in Weight of Oil Films during Setting.*

(All the Weights are expressed in Grams.)

Kind of Oil.	A (0.0 per Cent. Wax).		B (0.1 per Cent. Wax).		C (0.3 per Cent. Wax).		D (0.5 per Cent. Wax).		E (1.0 per Cent. Wax).	
Weight of Oil on Glass.	0.1535		0.2591		0.1677		0.1384		0.1800	
Time in Days.	Total Gain in Weight.	Gain per Gram of Oil.	Total Gain in Weight.	Gain per Gram of Oil.	Total Gain in Weight.	Gain per Gram of Oil.	Total Gain in Weight.	Gain per Gram of Oil.	Total Gain in Weight.	Gain per Gram of Oil.
1	0.0118	0.077	0.0149	0.058	0.0022	0.013	0.0014	0.010	0.0026	0.014
2	0.0194	0.126	0.0152	0.059	0.0028	0.017	0.0022	0.016	0.0041	0.023
3	0.0199	0.129	0.0161	0.062	0.0036	0.021	0.0022	0.016	0.0060	0.033
4	0.0187	0.121	0.0157	0.061	0.0035	0.021	0.0041	0.030	0.0071	0.039
6	0.0183	0.119	0.0161	0.062	0.0043	0.026	0.0057	0.041	0.0103	0.057
8	0.0165	0.107	0.0167	0.065	0.0047	0.028	0.0070	0.051	0.0129	0.072
11	0.0162	0.105	0.0188	0.072	0.0066	0.039	0.0095	0.069	0.0162	0.090
15	0.0158	0.102	0.0236	0.090	0.0096	0.057	0.0141	0.102	0.0206	0.114
18	0.0139	0.090	0.0240	0.092	0.0128	0.076	0.0150	0.109	0.0195	0.108
23	0.0136	0.088	0.0251	0.097	0.0172	0.102	0.0155	0.112	0.0202	0.112
30	0.0130	0.085	0.0240	0.092	0.0172	0.102	0.0149	0.108	0.0189	0.105
50	0.0118	0.076	0.0241	0.093	0.0167	0.100	0.0153	0.111	0.0187	0.104
159	0.0063	0.041	0.0189	0.072	0.0116	0.069	0.0149	0.108	0.0155	0.086

A consideration of these results leads us to the following conclusions:—

1. The addition of small quantities of paraffin wax to linseed oil retards the absorption of oxygen, and hence the setting of the oil. This retardation reaches a maximum with 0.3 per cent. of the wax. It is easy to see why addition of the wax should tend to retard the setting or oxidation of the oil, but it is less easy to understand why a maximum retardation should be reached with 0.3 per cent. of the wax, for one

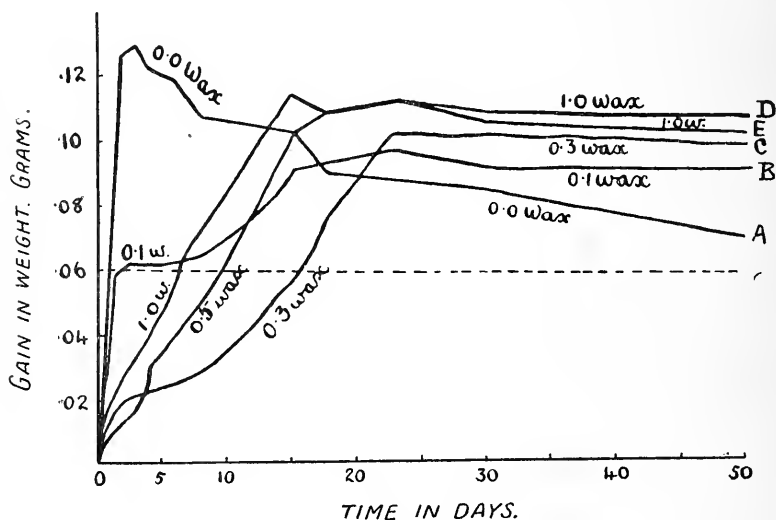


FIG. 5.—Showing the alteration in weight experienced by films of various mixtures of boiled linseed oil and paraffin wax on exposure to air.

would expect the rate of oxidation to decrease in direct proportion to the rise in percentage of paraffin. As we shall see in the next section, the oil films behave in an analogous manner in regard to their porosity to water vapour, so that there are evidently several factors concerned, which are as yet obscure.

2. At first the oil with 0.1 per cent. of wax behaves almost exactly like the pure oil, absorbing oxygen almost equally rapidly. The rate of oxidation then suddenly falls off, the maximum increase in weight being observed after twenty-three

days. This does not mean, however, that the film does not set for twenty-three days, for experiment showed that the film had hardened when about 0.06 gram increase in weight had taken place, as indicated by the broken line in the curve. According to this, therefore, we should expect the 0.1 per cent. oil to set almost as rapidly as the pure oil, then follow the 1 per cent., 0.5 per cent., and 0.3 per cent. oils in order, the last named being the slowest to harden. In point of fact the oils were found to set practically in this order when painted on to the iron test plates later.

3. After the maximum point has been attained, all the oils containing the wax exhibit a marked retardation in their rates of decomposition, the least loss in weight being experienced by the 0.3 per cent. oil. Evidently, therefore, by the addition of the wax we have greatly increased the chemical permanence of the oil. Here, then, we have scientific support for the now almost forgotten custom of grainers of putting a little wax into their graining colours. It was found as the result of centuries of experience that this small addition (usually bees-wax was employed, not paraffin wax) greatly improved the useful life of the work. But not understanding how that could be, the modern painter has allowed the custom to fall into disuse.

The question which now arises is—what is the best amount of paraffin wax to add? If a quick drying paint is essential, the 0.1 per cent. oil is undoubtedly the most suitable. But if the rate of drying is immaterial, the best results may be obtained with 0.3 per cent. of paraffin wax.

The results of the field tests carried out with these oils will be discussed in the next section.

The employment of the so-called “hungry” pigments, that is pigments which require a large amount of oil for easy working with the brush, tends towards the same goal. In this case the oil is soaked up into the pores of the pigment so that the atmospheric oxygen is but slowly absorbed. Whilst this means that the paint thereby produced is extremely bad to dry, yet when once dry it is correspondingly permanent, owing to the difficulty with which disintegration can take place. Carbon is a case in point, and all painters are familiar with the remark-

able permanency of lettering and signs executed with carbon blacks, and subsequently exposed to the most rigorous weathering in the smoky atmospheres of towns, and the bleak air of moor and mountain. The absorbent nature of the pigment likewise secures excellent contact between itself and the oil, so that the resulting paint is unusually impervious (*vide infra*).

2. *The Porosity of Oil Films.*

A few preliminary experiments were described in the author's Carnegie Scholarship Memoir last year (1911), in which the effect of paraffin wax upon the porosity of the oil towards water vapour was tested. An exactly similar series of experiments has now been carried out with oils A, B, C, D, and E. Filter papers soaked in these were allowed to set in a steam oven at 100° C. for twelve hours. After lying exposed to the air for a further eight days, they were tied over the mouths of small flasks containing 8 grams of calcium chloride, and placed under a bell jar round a dish of distilled water (as shown in the figure, *op. cit.*, p. 55). The flasks were weighed at varying intervals of time, with the results detailed in Table II.

It will be observed that the 0.5 per cent. oil is the least porous to water vapour, a larger percentage of paraffin yielding less favourable results. This confirms the observation to which attention was called in the earlier memoir, but an explanation is not easy to find.

Evidently, therefore, the most satisfactory mixture from the porosity point of view is the 0.5 per cent. oil, but the 0.3 and 0.1 per cent. oils only differ by relatively small amounts from this, whereas the porosity of the pure oil rises out of all proportion. In view, therefore, of the markedly superior setting power of the 0.1 per cent. oil, the probability is that in most cases this latter mixture will prove the most suitable to employ.

The great importance of studying the porosity of oil films will be evident when it is remembered that, in the absence of moisture, iron cannot rust. Hence, if an absolutely impervious medium could be found, a permanent cure for corrosion would be to hand.

TABLE II.—*Permeability to Water Vapour exhibited by Films of Linseed Oil containing varying percentages of Dissolved Paraffin Wax.*
(All the Weights are expressed in Grams.)

Time in Days.	A (0.0 per Cent. Wax).		B (0.1 per Cent. Wax).		C (0.3 per Cent. Wax).		D (0.5 per Cent. Wax).		E (1 per Cent. Wax).	
	Weight of Flask.	Increase.	Weight of Flask.	Increase.	Weight of Flask.	Increase.	Weight of Flask.	Increase.	Weight of Flask.	Increase.
0	37.1525	...	26.3540	...	29.3827	...	27.6835	...	39.9150	...
2	37.4222	0.4697	26.7005	0.4465	29.8885	0.3658	27.9753	0.2918	40.2214	0.3064
3	37.8433	0.6908	26.8602	0.5062	30.0239	0.4503	28.1145	0.4310	40.3674	0.4524
4	38.0136	0.8611	26.9820	0.6280	30.1428	0.5601	28.2215	0.5380	40.4772	0.5622
6	38.3855	1.2330	27.2530	0.8990	30.3015	0.8088	28.4595	0.7760	40.7225	0.8075
8	38.6926	1.5401	27.5455	1.1915	30.6603	1.0776	28.7183	1.0348	40.9907	1.0757
10	39.1995	2.0479	27.8436	1.4996	30.9350	1.3523	28.9785	1.2950	41.2610	1.3460
13	39.7327	2.4802	28.2356	1.8816	31.2973	1.7146	29.3205	1.6370	41.6205	1.7045

In order to put these oils to a practical test, both air and water tests are being carried out with plates of iron, and the results, in so far as they are at present attainable, are given in Tables III., IV., and V. These results are purely qualitative, but none the less reliable. All the plates were carefully weighed at the beginning of the tests, and observations are being recorded at regular intervals. When the plates have been exposed for a considerably longer time, and the films have thoroughly disintegrated, the plates will be scraped and weighed, and the quantitative results recorded.

From Table III., Experiments 2 to 6, it is seen that 0.3 and 0.5 per cent. oils give the best results; the 0.1 and 1 per cent. oils are almost as good, and are far superior to the pure oil alone, containing no dissolved wax. Experiments 7 and 8 illustrate the superiority of 0.1 per cent. oil over the pure oil when mixed with dried ferric oxide (Indian red). All these results refer to the action of the ordinary weather on the oil films. An examination of the results given in Tables IV. and V., Experiments 2 and 3, 4 and 5, 9 and 10, suffices to show that the 0.1 per cent. oil is decidedly superior to the pure oil when admixed with red lead or with Indian red to form a paint and continuously submerged under water.

3. *Electrical Insulation.*

This is a point of considerable importance, inasmuch as very serious galvanic action may occur between a pigment and the iron, leading to complete disintegration of the paint film and destruction of the iron through deep pitting. Galvanic action will not occur, however, in the absence of moisture, and would not therefore need to be taken into consideration in dealing with absolutely impervious paints. As these latter, however, have never been prepared, it is essential that we attempt to overcome this difficulty (1) by choosing such pigments as will not induce serious galvanic action; and (2) by rendering the film of oil in which the pigment is suspended as insulating as is compatible with elasticity, strength, and setting power, in order to render any galvanic action as weak as possible. To the former of these precautions we shall return

TABLE III.—*Results of Air Tests with Iron Plates painted with various Compositions, after Five Months' Exposure.*

[Only those results in the separate sections of this table are strictly comparable with one another.]

Plate No.	Date of Exposure.	Treatment of the Plate before Exposure.	Date of Examination.	Observation.	Condition No. ¹
1	1911 Aug. 28	Clean iron plate without paint.	1912 Feb. 3	Thoroughly corroded.	...
2	Do.	Plate painted on each side with 3·3 grams of pure linseed boiled oil.	Do.	The oil film is broken in several places, and slight corrosion of the iron evident over the whole of the surface.	1
3	Do.	Plate painted on each side with 3·3 grams of boiled oil containing 0·1 per cent. paraffin wax by weight.	Do.	One or two isolated places where rust has broken through the film. Far less corrosion manifest than in Plate 2.	3
4	Do.	Plate painted on each side with 3·3 grams boiled oil containing 0·3 per cent. wax.	Do.	This plate is in a slightly better condition than Plate 3.	4
5	Do.	Plate painted on each side with 3·3 grams boiled oil containing 0·5 per cent. wax.	Do.	Similar to Plate 4.	4
6	Do.	Plate painted on each side with 3·3 grams boiled oil containing 1 per cent. wax.	Do.	Similar to Plate 3.	3
7	Sept. 14	Plate painted on each side with 5 grams of paint consisting of 100 grams dry ferric oxide in 160 grams of pure boiled oil.	Do.	Evidences of slight corrosion under the paint film.	1
8	Do.	Exactly similar to Plate 7, but paint contained in addition 0·1 gram paraffin wax per 100 grams of oil.	Do.	Evidence of corrosion less apparent than in Plate 7.	2

¹ This number has been arrived at by calling the most corroded plate 1, and grading the other plates accordingly by their respective *appearances*. No actual weighings are involved. The higher the number the better the protection.

TABLE IV.—*Results of Small Water-tank Tests with Iron Plates painted with various Compositions after Four Months' Exposure.*

Plate No.	Date of Exposure.	Treatment of the Plate before Exposure.	Date of Examination.	Observation.	Condition No. ¹
1	1911 Sept. 15	Plate painted on each side with 2.5 grams of paint containing 100 grams fine rouge in 160 grams of pure boiled linseed oil.	1912 February	Same condition as Plate 2.	1
2	„ 13	Plate painted on each side with 2.5 grams of paint containing 100 grams rouge (fine and coarse mixed) in 160 grams of pure boiled linseed oil.	Do.	Slight corrosion evident under paint surface.	1
3	„ 13	Plate painted on each side with 2.5 grams of mixed rouge paint, same as Plate 2, save that 0.1 gram paraffin wax was added to each 100 grams of oil.	Do.	This plate is in slightly better condition than Plate 2.	2
4	„ 6	Plate painted on each side with 2 grams of pure boiled linseed oil.	Do.	No apparent difference between the two plates.	...
5	„ 6	Plate painted on each side with 2 grams of linseed oil containing 0.1 gram paraffin wax per 100 grams of oil.	Do.		...
6	„ 14	Rusty iron plate dried at 100° C. and free from scale painted with 2.5 grams mixed rouge paint (see Plate 2) on each side.	Do.	Same condition as Plate 2.	1
7	„ 13	Plate painted on each side with 2.5 grams coarse rouge paint containing 100 grams coarse rouge in 160 grams of pure boiled oil.	Do.	Same condition as Plate 2.	1

¹ See note to Table III.

TABLE V.—*Results of Large Water-tank Experiments with Iron Plates.*

Plate No.	Date of Exposure.	Treatment of the Plate before Exposure.	Date of Examination.	Observation.	Condition No. ¹
9	1911 Sept. 18	Plate painted on each side with 3.5 grams red lead paint containing 50 grams red lead per 5 grams boiled oil.	1912 February	Evidences of slight corrosion under the paint film.	1
10	Do.	Plate treated similarly to Plate 9, but the paint contained in addition 0.1 gram paraffin wax per 100 grams boiled oil.	Do.	Plate slightly less corroded than Plate 9.	2
11	Oct. 4	Plate painted on each side with 2 grams of coarse rouge paint containing 100 grams of coarse rouge per 200 grams of oil.	Do.	Plates 11-16 all in similar condition. Iron slightly corroded under painted surface.	1
12	Do.	Plate painted on each side with 2 grams of fine rouge paint containing 100 grams of fine rouge per 200 grams of oil.	Do.		1
13	Do.	Exactly similar to Plate 11.	Do.		1
14	Do.	Exactly similar to Plate 12.	Do.		1
15	Do.	Exactly similar to Plate 11.	Do.		1
16	Do.	Exactly similar to Plate 12.	Do.		1
17	Oct. 27	Plate painted on each side with 4 grams of mixed rouge paint containing 100 grams of mixed (fine + coarse) rouge per 200 grams of boiled oil.	Do.	Paint surface nearly perfect. Considerably better condition than Plates 11-16.	2

¹ See note to Table III.

TABLE V.—*Continued.*

Plate No.	Date of Exposure.	Treatment of the Plate before Exposure.	Date of Examination.	Observation.	Condition No.
18	1911 Oct. 27	Rusty plate dried at 100° C., treated in a precisely similar manner to Plate 17.	1912 February	Same condition as Plate 17.	2
19	Do.	Exactly similar to Plate 17.	Do.		2
20	Do.	Exactly similar to Plate 18.	Do.		2
21	Do.	Plate painted on each side with 2 grams of mixed rouge paint (see Plate 17).	Do.	Same condition as Plates 11-16.	1
22	Do.	Exactly similar to Plate 21.	Do.		1

in the sequel when discussing the most suitable pigments for paints. The second precaution is facilitated by the addition of paraffin wax to the oil, inasmuch as the wax, being a solid hydrocarbon, is well known to be remarkably resistant to the passage of electric or galvanic currents. Here, then, we have a third and potent reason for the employment of this substance in our paints.

II.—THE PHYSICAL CONDITION OF THE PIGMENT.

Under this heading a large variety of points remain to be considered, the more important being:—

1. The size of the pigmentary particles.
2. The porosity of the particles themselves.
3. The colour.
4. Solubility.
5. Galvanic activity.
6. Dryness or hygroscopicity.

We shall proceed to deal with each of these as the experiments allow.

1. *The Size of the Pigmentary Particles.*

There can be no reasonable doubt that coarse pigmentary particles are quite unsuitable for painting purposes. This is well illustrated by numerous examples, the classical one being the deterioration of the steelwork in the New York Underground Railway.¹ This had been cleaned and painted with a mixture of 19 parts by weight of red lead and $4\frac{1}{2}$ parts of linseed oil; in addition to this, the more exposed places received a coat of white lead. After $2\frac{1}{4}$ years cracks were observed in the paint films, and by means of a knife, large sheets of paint could be removed, exposing the rusted metal beneath. Microscopic examination proved that the cause lay in the coarseness of the particles of lead oxide, resulting in insufficient combination between the oil and the pigment, so that the paint was abnormally porous to moisture.

It will be clear that, in the case of the inert fragments, the degree of contact between the oil and the pigment is influenced by two factors, namely (1) the size of the pigmentary particles, and (2) their porosity.

Here we shall deal with the former property, as the latter is considered in the next section.

It is not generally realised that unit weight of fine pigmentary particles will possess an enormously greater superficial area than the same weight of coarse particles, and hence will mix more thoroughly, in proportion, with a liquid vehicle.

Thus, for example, suppose we take a pigmentary particle of radius r_1 and grind it to n particles of radius r_2 . Assuming for ease of calculation that the particles are perfect spheres, and that nothing is lost during the process, the volume must remain unaltered. Hence

$$\frac{4}{3}\pi r_1^3 = \frac{4}{3}\pi n r_2^3$$

$$\text{and} \quad n = \frac{r_1^3}{r_2^3} \quad \dots \dots \dots (1)$$

Considering now the surface area of the particles we have

$$\frac{\text{Area of original particle}}{\text{Total area of small particles}} = \frac{4\pi r_1^2}{4\pi n r_2^2} = \frac{r_1^2}{n r_2^2}$$

$$= \frac{r_2}{r_1} \text{ (substituting for } n \text{ from equation 1) } \quad (2)$$

¹ *Bayerisches Industrie und Gewerbe-Blatt*, 1906, No. 30.

Hence the superficial areas of the particles are inversely proportional to their radii or their diameters. Now, in a well-ground pigment the particles may be expected to vary from 0.002 millimetre to 0.026 millimetre in diameter, and it follows that if two paints were prepared from equal weights of the smallest particles and the largest particles respectively, the liquid vehicle in the former would be some thirteen times more thoroughly in contact with its pigment than the latter, and its stability and spreading power would thereby be greatly increased. In addition to this, the particles may be more closely packed together, thus rendering the paint less porous to oxygen and water vapour.

Clearly, therefore, the finer the pigment, the more valuable is the resulting paint from a protective point of view, and this is no doubt one of the main reasons for the success attending the use of pigments condensed from vapours, such as the Purex basic lead sulphate, in the painting of iron and steel.

In this connection, however, two questions of importance arise, namely :—

1. Is it advisable to have the pigmentary particles all of one size? and
2. To what extent should the size of the particles be reduced?

In reply to the former of these questions it would appear that we do not need to have all the particles of one size, but there must be a fair percentage of very small particles in order to fill up the gaps between the larger ones, and thus to render the film impervious. On the other hand, very large particles must clearly be avoided, for reasons already given.

The answer to the second question is less easy to give, as we have several important factors to consider, two of the chief being as follows :—

(a) The finer the pigment, the greater is the spreading power; and if this is increased beyond a certain limit, the “body,” or power of hiding the under surface from view, becomes too weak for practical purposes. Of course this may be overcome by applying several coats of paint, but the cost thereby entailed would in most cases be prohibitive.

(b) The cost of grinding a pigment beyond a certain limit

increases out of all proportion to the reduction in size of the pigmentary particles. It may therefore be much cheaper to paint a steel structure twice with a good average paint than to protect it once with an excessively finely ground paint.

The probability is that the medium course is the best—as in most other cases—and that, by employing a really first-class pigment ground thoroughly well according to the present standard of the best firms, the most satisfactory results will accrue both as regards the price of the paint and the preservation of the metal. But this conclusion has yet to be confirmed by the rigid results of direct experiment.

From the above it will be clear also that in judging of the relative merits and demerits of various pigments, the tests employed should be made with similarly sized particles; and herein undoubtedly lies the source of some of the conflicting results obtained by painters. If, for example, the results already mentioned as obtained with lead oxide paint in the underground railway at New York were compared with similar work executed with good average red oxide (ferric oxide) paint, the latter pigment would be pronounced far superior for the purpose. But it would be easy to arrange for a precisely opposite result by using coarse ferric oxide and fine lead oxide. The above is, of course, an extreme case, but shows that unless the painting is carried out in a strictly comparable manner, the results obtained may not be regarded as comparable. Herein lies, as it seems to the author, a serious source of weakness in the numerous paint tests which are being carried out in America, and which have been so frequently brought before our notice by Dr. Cushman and others. So far as can be ascertained, no attempts have been made to secure pigments of equal fineness.

In order to throw some light on the points just discussed, some test plates were painted with two grades of ferric oxide respectively, and with a mixture of these grades. They were then submerged in the water tanks. (See Experiments 1, 2, and 7; 11, 12, 13, 14, 15, 16, 21, and 22, Tables IV. and V.).

The two grades of ferric oxide were obtained by repeated

levigation, the size of the particles being calculated from the formula given by Stokes—

$$v = 2ga^2(6 - \rho)/9\eta$$

where

v = velocity of falling particles in centimetres per second.

6 = density of pigment (taken as 3).

a = radius of particle required.

ρ = density of the liquid, in this case, water, and practically unity.

η = coefficient of viscosity of the liquid (water is 0.011).

Hence it is easy to show that the diameter of the pigmentary particles in suspension in water after standing at a given depth for t seconds cannot be greater than

$$a \text{ (diameter)} = \sqrt{v/10} \text{ millimetres (approximately).}$$

The coarsest particles were those which settled from distilled water at a depth of 7.5 centimetres during 12.5 minutes. By repeatedly treating in this way until the supernatant liquid, which was poured off every time, was quite clear, all the smaller particles were removed, and the sediment consisted only of those of greater diameter than 0.01 millimetre.

The lighter particles which had remained in suspension were allowed to settle in a separate tank, and levigated repeatedly in a precisely similar manner at a depth of 10 centimetres during sixty minutes. The sediment consisted of particles ranging from 0.005 to 0.01 millimetre in diameter. This portion was rejected, being exceedingly small.

The first particles which had remained in suspension were now allowed to settle for twenty-four hours, and their diameters were less than 0.005 millimetre, and constituted about one-twentieth of the original weight of pigment. Some of the original ferric oxide, the coarsest levigated particles, and the finest were now dried thoroughly in the steam oven and intimately ground with boiled linseed oil in a mortar. The plates were painted with these mixtures as indicated in the tables. In considering the results, however, it must be borne in mind that the above calculations of the sizes of the pigmentary particles are only approximate, for they are based on the assumption that the particles are all spheres and regular in shape. This, of course, is not actually the case, but probably the divergence will not be any more serious than the average experimental error in carrying out the tests.

2. *The Porosity of the Pigmentary Particles.*

In the previous section it has been assumed that the pigmentary particles are regular, non-porous spheres, and it has been shown that the smaller these particles are, the more perfect is the contact between them and the liquid vehicle. Inasmuch as there comes a practical limit to the state of fineness of the pigment, for reasons already detailed, the question arises as to whether or not it is possible to improve the paint by increasing the area of contact without necessarily reducing the size of the particles. This may be accomplished by the employment of porous pigments, such as the carbon blacks, which absorb a large amount of oil and yield an extraordinarily thorough mixture or paint. The disadvantage of such paint, however, lies in its slow rate of setting, but this may be largely overcome by a due admixture of a drying pigment, such as red lead. Ferric oxide is likewise a "hungry" pigment, and a mixture of these three pigments is strongly advocated by certain bridge-painters as yielding the most satisfactory results in a humid atmosphere.

Inasmuch as porous pigments are, from their very nature, unusually hygroscopic, care must be taken to dry them before use. This point is adverted to in a later section (§ 6).

3. *The Colour of the Pigment.*

This is a property about which practically nothing is known, but some as yet immature experiments are now in progress with a view to throwing light on this important problem. A good deal has been written about the subject, but conclusions based on experiments with different coloured pigments which have likewise a different chemical composition and physical nature, are influenced by so many other factors—as the reader of this memoir will observe—that nothing very reliable can be deduced from them. Experience seems to indicate, however, that the darker the pigment, the more permanent the oil film, other things being equal; and the explanation given is that the dark pigments absorb the actinic rays of light, and thus

prevent their stimulating—as they are well known to do—the disintegrative oxidation of the oil.

4. *The Solubility of the Pigment.*

This is a point of considerable importance in view of the fact that our paints are not impervious to moisture. A very soluble pigment would be useless, as it would soon wash out of the paint, and leave a honeycombed and weakened film of oil on the painted metal. Further, the soluble material would probably attack the metallic surface and stimulate its corrosion.

But very few pigments are as insoluble in water as carbon and barium sulphate, and if we must employ such as are slightly soluble, preference must be given to those whose aqueous solutions are least corrosive. In this respect the palm must certainly be given to the chromes, for aqueous solutions of chromates tend to render iron passive and thus to inhibit corrosion. Other pigments, such as basic lead chloride (Turner's yellow, &c.), verdigris, &c., are clearly unsuitable—a point that has been recognised for some years in practice, and is emphasised by the fact that these and many similar pigments are now practically obsolete, whereas the chromes are receiving increasing favour. This constitutes one of the scientific foundations for the classification of various pigments into three groups, namely, Inhibitors, Indeterminates, and Stimulators, as adopted by Dr. Cushman, about which there have been so many disputes. The fact of the matter is, this factor has been pushed too far, and other counteracting influences have been overlooked. (See Section 5.)

5. *The Galvanic Activity of the Pigment.*

It is now well recognised that many substances accelerate the corrosion of iron when placed in contact with it in a moist condition. Tin and copper are cases in point. Since our paint films are not perfect insulators, it is obvious that, from this point of view, the most suitable pigments will be such as stimulate destructive galvanic action to the least extent.

These would appear to be the chromes and the more highly electro-positive metals, such as zinc and aluminium, which latter are now being used in considerable quantities as pigments. The former of these, namely the chromes, owe their beneficial influence, as we have seen, to their solubility in water leading to the passivification of the iron. The latter owe their protective value to the greater ease with which they undergo oxidation than iron. Lampblack and graphite, on the other hand, take a low place in this connection, as they tend to cause high galvanic activity. Cushman very rightly classifies these amongst the stimulators of corrosion, and for this reason their use has been condemned.

This, however, is illogical, for galvanic activity is only one of the many factors to consider. For example, the protective action of the chromes may well be counterbalanced by the greater porosity produced in the oil films by the gradual dissolving out of the pigment. Similarly, in the case of the zinc and aluminium pigments, these oxidise themselves in saving the iron from corroding, and the expansion thus produced within the pores of the paint may well lead to disintegration of the paint, thereby more than neutralising any beneficial action. On the other hand, the carbon blacks are excessively insoluble, so that they neither swell nor dissolve away; they are porous, and thus associate themselves very intimately with the oil; and finally, they are dark and absorb the destructive actinic rays of light. It is always possible, therefore, that in the actual testing these good points may outweigh the single disadvantage of destructive galvanic activity; and these are results which can only be ascertained by actual trial. Experiments are in progress with a view to throwing light on this subject, and the increasing favour with which graphite paints are being received would seem to indicate that our argument is worthy of consideration.

6. *The Hygroscopicity of the Pigment.*

The fatal consequences of applying a wet paint to any surfaces are too well known to need discussion, but painters frequently overlook the fact that many pigments are very

hygroscopic, and until ground in oil should be kept in dry places. In fact, before grinding in oil they should be dried in an oven at, say, 100°C . It is quite a usual thing for the carbon blacks to contain 6 per cent. of water, and Hurst¹ gives numerous analyses in which this amount of moisture was found to range from 28 per cent. to the incredible extent of 45.5 per cent. What wonder if a pigment of this nature is found to compare unfavourably with pure dry red lead or ferric oxide.

III. THE CHEMICAL CONDITION OF THE PIGMENT.

This branch of our subject resolves itself into three parts, namely:—

1. The chemical permanence of the pigment towards air, moisture, light, &c.
2. The action of the pigment on oil.
3. The action of the pigment on iron.

In this connection there remains but little to be said. The first and third of the points have already been discussed in preceding sections; with regard to the second, but little of definite value is at present known.

IV. THE CONDITION OF THE IRON SURFACE TO BE PAINTED.

Two points require emphasis in this connection, namely:—

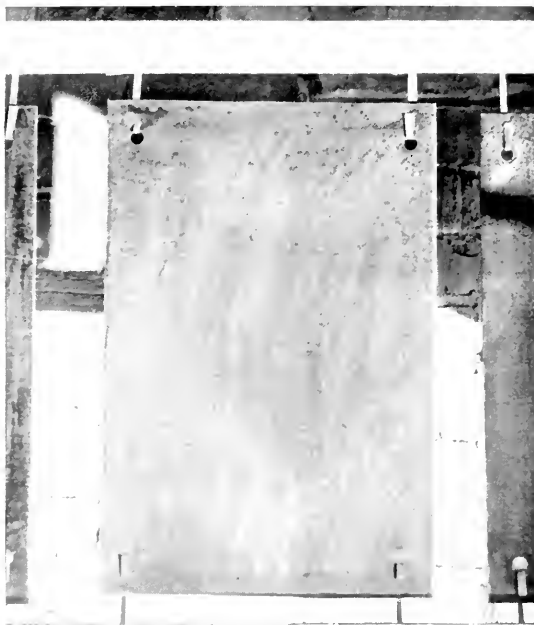
1. The metal should be dry; and
2. Free from adhering rust.

The former of the points scarcely calls for emphasis here, as it is nowadays so well recognised by painters.

With regard to the latter point, it is always found that a rusted surface when painted yields unsatisfactory results, so that the careful painter removes the rust prior to the application of paint. It occurred to the author, however, that a slight coating of rust, absolutely free from caking and lumps, might be an advantage rather than otherwise, if perfectly dry, for two reasons:—

¹ Hurst, "Painters' Colours, Oils, and Varnishes," Griffin & Co., 1906.

PLATE 1



Method of Suspension of Plates.

1. Fine rust is practically a pure ochre, very free, in the case of wrought iron and steel, from silica. Hence the surface is very absorbent, and if painted with a good coating of thin paint a similar result may be expected as by first laboriously cleaning the metal and then painting with a thicker paint, that is, one containing more pigment in proportion to oil than the former.

2. If the iron surface is sandpapered down it is made much smoother, and its area is reduced to a minimum. If, however, the rust is left on as a thin coating, the underlying surface of metal in contact with the rust is slightly pitted and uneven. Hence when the paint is applied it has a larger surface to grip, and its tenacity will thereby be increased in proportion.

On the other hand, the particles of rust are often much coarser than those of the pigment, and this may in itself suffice to counterbalance any advantages gained in other directions.

In order to put these conclusions to the test practically, three plates were allowed to rust by exposure to weather, and when a thin layer of rust had been formed (after about a week), the plates were thoroughly dried in a steam oven at 100° C., and finally painted with rouge whilst the rust was still adhering. On drying (setting) these plates were placed in the water tanks alongside others painted in a precisely similar manner, but upon their bright (not rusty) surfaces. (See Experiments 6 and 2; 18, 20; and 17, 19.) In actual practice, of course, the difficulty lies in rendering the iron surfaces perfectly dry.

V. THE METHOD OF APPLICATION OF THE PAINT.

It is universally recognised that two medium coatings of paint are far superior to one very thick coat, even although the total weight of paint applied in the first case is no greater than that in the second.¹

This opens up the question as to what length of time

¹ Compare the results of Liebreich and Spitzer, *Zeitschrift für Elektrochemie*, vol. xviii. p. 94.

should be allowed to elapse between the application of the first and second coats respectively. The answer to be given depends both upon the rate at which the paint normally sets, the thickness of the coat applied, the temperature of the air, and a variety of other minor factors. It is desirable, however, if the best results are to be obtained, that sufficient time be given to allow the first coat to attain to the condition represented by the point B in Fig. 4, for up to this point the change in weight and volume of the film is relatively large, but after this point it becomes slow—increasingly slow when protected by a second paint film. Consequently it then forms a more stable foundation for the second film. The probability, therefore, is that the best results will be obtained if the first coat is allowed to stand for from two to three times as long a period as it takes to set (that is, to reach the point D). It will then have arrived at the condition represented by B, and be ready for a second coat.

APPENDIX.¹

The first six plates mentioned in Table III. were examined, cleaned, and weighed on 24th April 1912, after an exposure of nine months to the weather. The cleaning was effected by soaking in caustic potash solution, which removed the film of oil and loosened the rust. The plate was then well washed and scrubbed with water, dried and scrubbed with methylated spirits, and finally any rust still adhering was gently scraped away with a penknife. The figures in the last column are obtained by taking the protection afforded by linseed oil (namely, 100/5·3) as the standard unit of protection, namely 1, and expressing the protective actions of the other mixtures in terms of this standard. Thus, for example, the protection factor of the oil containing 0·1 per cent. paraffin is—

$$\frac{100}{3\cdot6} \div \frac{100}{5\cdot3} = \frac{5\cdot3}{3\cdot6} = 1\cdot47;$$

and so on. In view of the numerous paints—some good and some useless—now pushed on to the market as preventers of

¹ Received May 6, 1912.

rusting, it seems desirable to adopt some such method of comparison as this, in order that the consumer may know the relative values of the paints he is purchasing. Owing to the variations in the properties of even pure linseed oil—as is inevitably the case with a natural product—the author is not prepared to suggest that it be taken as the standard permanently, but wishes to call attention to the urgent need of establishing some recognised protection factor for paints destined to be applied to iron and steel surfaces.

Plate No.	Observed Condition of Plate.	Initial Weight of Plate. Grammes.	Loss in Weight. Grammes.	Relative Corrosion.	Protection Factor of Oil.
1	Metal thoroughly corroded . .	812.7	66.1	100	...
2	Oil film thoroughly disintegrated	815.6	3.5	5.3	1
3	Much better surface than No. 2 .	777.7	2.4	3.6	1.47
4	Surface very slightly better than } No. 3 }	811.0	1.6	2.4	2.2
5	The best surface of all	799.9	1.6	2.4	2.2
6	Exactly similar to No. 4 . . .	778.3	1.3	1.9	2.8

From the above table we learn two important facts:—

1. The surface of the paint film does not always give a correct idea of the extent of the corrosion (see Nos. 4, 5, and 6).
2. The addition of a small quantity of paraffin wax to linseed oil greatly enhances its protection factor.

THE CONSTITUTION OF THE SULPHIDE ENCLOSURES IN IRON AND STEEL AND THE DESULPHURISATION PROCESS.¹

BY G. RÖHL, DIPL.ING. (FREIBERG, SAXONY), CARNEGIE SCHOLAR.

THE microscopical investigation of the internal structure of the iron-carbon alloys, and particularly of the steels, has shown that not only does wrought iron, as has already long been known, contain slag enclosures (a fact which is at once explained by its production in a pasty condition), but that slag deposits occur in most ingots of mild steel, even though to so small an extent that their presence was previously frequently overlooked or ignored. There is also the fact, to which Rosenhain has already drawn attention,² that these enclosures generally appear on the broken test-pieces simply as diminutive black specks easily escaping observation, since the enclosures, in consequence of their plasticity, have generally undergone elongation perpendicular to the surface of rupture before breaking. It should be specially mentioned here that in the case of rolled and wrought material, longitudinal sections (*i.e.* parallel to the direction of the main dimension) are almost indispensable.

During the last few years increased attention has been paid to these slag enclosures, the following workers having occupied themselves with the question:—

ANDREWS.—*Engineering*, vol. xlii., July 10, 17, 24, 1896.

LE CHATELIER.—“Sulphide of Iron, its Properties and its Condition in Iron.” *Bulletin de la Société d'Encouragement*, September 1902.

ARNOLD.—“The Influence of Sulphur and Manganese on Steel.” *Journal of the Iron and Steel Institute*, 1903, No. I. p. 141.

STEAD.—*Iron and Steel Magazine*, vol. ix., No. 2, p. 105.

HOWORTH.—“Greenish-coloured Markings in the Fractured Surfaces of Test-pieces.” *Journal of the Iron and Steel Institute*, 1905, No. II. p. 301.

¹ Received February 8, 1912.

² Reports to the International Association for Testing Materials, 1909, No. 5.

- HEYN and BAUER.—*Bericht des Materialprüfungsamtes*, 1906, vol. xxiv. p. 233.
 LAW.—“Non-metallic Impurities in Steel.” *Journal of the Iron and Steel Institute*, 1907, No. II. p. 94.
 ROSENHAIN.—*International Association for Testing Materials*, 1909, No. 5.
 MATWIEFF.—*Revue de Métallurgie*, 1910, p. 447.

The expression “slag enclosures” may simply have been borrowed from the phenomenon in wrought iron. Its use in that connection is fully justified since it is actually a question of the slag particles of the refining process which have been retained between the iron crystals which form in the pasty condition. The case is quite different, however, with mild steel, where the enclosures, briefly termed “slags,” may be formed partially by particles from the slag formed during the process; or they may have been in some cases constituents of the fireproof materials with which the steel bath comes into contact; or derived from the ladles and casting channels. The chief source, however, will be the reduction products of the steel bath just previous to and during solidification.

The term “non-metallic enclosures,” as first used by Heyn and Bauer, would seem to be the most accurate to use. Law also (*loc. cit.*) designates the enclosures as “non-metallic impurities.” The chief non-metallic enclosures which may occur in steel are: sulphides of iron and manganese, ferrous and manganous oxide, aluminium oxide, and silicates of iron and manganese. From the term “non-metallic enclosures” must be excluded all the alloy products in steel which are to be regarded as staple solutions, as mixed crystals of elements or combinations with metallic iron, such as phosphide-enrichment in steels rich in phosphorus. As mixed crystals of iron these have metallic properties.

It is clear that the non-metallic enclosures must have a more or less marked influence on the properties of the materials, according to their nature or occurrence, and whether brittle or plastic, or whether occurring as a flattened deposit or as globules. These enclosures may give rise to dangerous flaws in the material, leading to breakages.

Special attention should be paid to the internal structure of these alloys, and it is easy to understand that an ordinary iron and steel analysis may afford but little information as to the

properties of these materials. Law has very correctly pointed out the inadequacy, in this respect, of the data given by ordinary analyses which ignore the structural constituents practically entirely. He states (*loc. cit.*): "In view of the importance of this question the author is strongly of opinion that the ordinary chemical analysis should be modified to include this information. No responsible chemist would report the carbon in a cast iron without distinguishing between the combined and the graphitic conditions, and it is surely of almost equal importance that we should know whether the silicon occurs as silicide in solution, in which condition it confers valuable properties upon the steel, or whether it occurs as silicate, in which condition it is never desirable and frequently dangerous."

The analysis is similarly silent as to the form and combination in which, say, sulphur occurs; and it is in this case at least as important to know whether the sulphur occurs as FeS or as MnS. There is no doubt that the qualitative and quantitative analysis of the individual structural constituents of the metallic alloys will in the future form one of the chief problems of metallurgical chemistry, a fact already emphasised by Martens.¹

The slag enclosures, as has already been said, are not the least important of these structural constituents in steels. The question first of all is to be able with rapidity and certainty to recognise the enclosures occurring in a steel, to identify them according to their nature, and, if possible, to discover methods for their quantitative analysis.

If once ways and means are found of determining qualitatively and quantitatively, and in a manner free from objection, the nature of the slag enclosures in steel, it will be possible to institute further observations for the future in connection with steel investigations. Subsequently it will be possible, from an accurate knowledge of the nature of the enclosures, to draw conclusions as to their origin, and, finally, to prevent the possibility of their formation, or, at least, to restrict it.

The object of this study will therefore be to carry out the investigations mentioned above on the metallic enclosures in

¹ *Österreichischen Zeitschrift für Berg- und Huttenwesen*, vol. xli. p. 619.

steel which appear to be the most important—the sulphide enclosures; for it appears most essential to be able to determine, in a given case, whether the sulphur is present as ferric or manganic sulphide, as the two sulphides have fundamentally different properties which are not without their influence on the mother-metal. FeS is extremely brittle and somewhat hard, and is thus an unwelcome concomitant of iron when the latter is cold worked or when the material is under strain at ordinary temperature. In addition it has, as a eutectic in iron, the lowest melting point, fusing, as Le Chatelier has already shown, at 980°C ., a temperature at which iron is only red hot. The individual iron grains therefore naturally lose their internal connection and a disintegration of material occurs, resulting in hot brittleness. On the other hand, however, MnS , apart from its endeavours to separate owing to the high melting point, is not brittle but quite plastic at forging heat, and even at ordinary temperatures capable of undergoing a certain degree of deformation without fracture.

Arnold has already stated, as a result of his observations (*loc. cit.*): “Iron sulphide is very dangerous to steel, manganese sulphide being fairly harmless on account of its refractory nature and plasticity.” Le Chatelier (*loc. cit.*) also says: “It is known that manganese reduces to a great extent the deleterious effect of sulphur on iron.”

It was also hoped by the close study of these sulphide enclosures and their constitution to obtain valuable information as to the desulphurisation processes in the steel bath and the conditions favouring them.

In order to obtain more accurate knowledge of the constitution of the sulphide enclosures, the investigations were extended to the determination of the system $\text{FeS} - \text{MnS}$, regarding which the literature on the subject gives no information. Investigations on the influence of manganese sulphide on the $\text{Fe} - \text{FeS}$ -eutectic follows on the above subject, as does also the investigation of the behaviour of the different stages of manganisation of the sulphides when they are in considerable excess of pure and carburised iron.

It appeared at the outset of the investigation hopeless to

adopt the method of separating the sulphide enclosures from the mother-metal in view of the ease with which the sulphides are decomposed by acids or oxidised by bromine, &c. It may certainly be said to be hardly ever possible to attain a quantitative isolation of the smallest sulphide enclosures. This object seemed more likely to be attained for oxide and silicate enclosures, although no unobjectionable method of separation from the metal is known at present, even for the slag enclosures occurring in much more compact masses in ingot iron.¹ It is presumed that the solvent for iron attacking the microscopic enclosures in steel will be considerably more energetic than it is in the case of wrought iron, giving results in the chemical analysis of the residuum which it is quite impossible to check, and which are often left to mere chance. It has, however, been shown by Schneider (*loc. cit.*), that even well-diluted acids exert an appreciable effect on the slag enclosures. It may be mentioned that attempts have been made to adopt even this method for the purpose of deriving information as to the composition of the enclosures. Thus, Howorth² has found it possible to isolate a residuum from samples of steel by means of dilute nitric acid, these samples showing all shapes and round holes containing sulphides. The following was the composition of this residuum:—

	Per Cent.
SiO ₂	46·61
MnO	48·08
Al ₂ O ₃	3·39
FeO	1·92

It is further stated in the same paper that 0·02 per cent., and on another occasion 0·27 per cent., of silicate enclosures of an approximate composition MnO, SiO₃ were isolated from bad steel, whereas in a good plate a quantity of only 0·05 per cent. residuum of the formula (MnO)₂(SiO₂)₃ was obtained.

It appears feasible for studying the constitution of the sulphide enclosures to proceed in a synthetic manner, that is, to produce in as pure a manner as possible the sulphides of iron and manganese forming non-metallic enclosures in steel,

¹ Cf. Ledebur, *Handbuch für Eisenhüttenlaboratorien*; and Schneider, *Österreich. Zeitschrift für Berg- und Hüttenwesen*, vol. xlviii. p. 257.

² *Journal of the Iron and Steel Institute*, 1905, No. II. p. 301.

and then incorporating the enclosures separately or together in a liquid iron bath of the greatest possible purity in different degrees of concentration.

The sections resulting from these meltings are then submitted to a stringent examination under the microscope, special attention being directed to the discovery of characteristic etching or colouring reagents, with the aid of which it is possible to secure certain recognition of the sulphide character of the enclosures, and to differentiate between iron sulphide and manganese sulphide enclosures.

In view of the exclusion of any impurities likely to be caused by gases of combustion (and the attendant danger of the absorption of sulphur and carbon), the type of furnace selected was one in which an electric current was used for generating the heat. It is possible to regulate the temperature with rapidity and certainty. It is also necessary to take into account the following points: The furnace must admit of attaining temperatures of 1600° to 1700° C. without trouble, and of working in an inactive gaseous atmosphere. It was thus impossible to use platinum resistance furnaces, even though they enable work to be done conveniently *in vacuo* or in a definite gas atmosphere. Kryptol furnaces may be used, but they easily lead to disturbances, even in the best melting tubes, on account of local arcing at high temperatures. The meltings were finally carried out in a transformer carbon tube furnace, enabling 40 grammes of the purest iron to be melted down in a few minutes. At a pressure of 6 volts, and with a current of 400 to 450 amperes, temperatures of 1700° C. and over were easily attained with the furnace. It should be mentioned that the oven was driven by a motor transformer which permitted of transforming the direct current of the supply station, at 440 volts 33 amperes, to 6 volts 1500 amperes.

The material to be melted was contained in Tammann tubes of fireclay, the latter being inserted in the furnace, the operation of melting being conducted in a nitrogen atmosphere to prevent oxidation. This nitrogen was taken from a cylinder, washed with an alkaline solution of pyrogallie acid, dried with concentrated sulphuric acid, and introduced from

the top into the melting tube, which was covered by an asbestos protecting disc.

PRODUCTION OF THE MELTED COMPONENTS IN A CHEMICALLY PURE STATE.

The Iron.—At the outset great care was paid to securing material as pure and unobjectionable as possible, since it seemed desirable in the microscopical examination of the meltings that the components whose behaviour was to be determined should be present in as pure a state as possible when submitted to characteristic etching substances.

It is well known, of course, that iron eagerly absorbs traces of other elements, metals or metalloids, forming solid solutions, and hence great care must be devoted to the selection of the iron used.

It may be mentioned here that in similar investigations on the slag in wrought iron, Matwieff (*loc. cit.*) commenced with puddled iron, embodying therein the components to be investigated. The metallographical results for the components afterwards added may, however, easily be rendered obscure by the numerous slag enclosures already in the puddled iron itself.

Commercial metallurgically-produced pure iron frequently contains greater or lesser quantities of other elements, especially carbon; and for this reason it was not possible to use even the so-called flower wire, such as is frequently used in the titration of the permanganate solution in ironworks laboratories.

It was finally decided to employ for the smelting experiments an electrolytic iron, placed on the market by the Langbein-Pfannhauser-Werke, Leipzig-Sellerhausen. This iron is produced in a large-scale experimental plant, is of first-rate purity and uniform quality, and is sold commercially up to 5 millimetres thickness, having a beautiful, compact surface of a metallic silver-white lustre. This electrolytic iron shows a high degree of purity. The result of the analysis was as follows:—

	Per Cent.
Sulphur	0·006
Silicon	0·003
Phosphorus	trace
Manganese	absent
Carbon	absent

In order to rid the iron of the hydrogen (invariably present) it was only necessary to anneal the former for a short time *in vacuo* by placing it in a porcelain tube in a platinum resistance furnace kept at red heat, the hydrogen being completely removed in this manner. The iron, which was very hard and extremely brittle before annealing, on account of the hydrogen content, showed great ductility and softness after treatment. Meltings of this electrolytic iron showed only a uniform ferrite surface on the section after etching with alcoholic hydrochloric acid.

Ferrous Sulphide.—It was quite impossible to use commercial ferrous sulphide for the smelting experiments, since, as Le Chatelier (*loc. cit.*) and Ziegler¹ have already shown, the sulphide on an average possesses some free iron and a not inconsiderable percentage of ferrous oxide, which may amount to 25 per cent. The sulphur content generally falls below 30 per cent., while pure ferrous sulphide requires 36·48 per cent. sulphur.

A pure sulphide was made in the following manner for the purpose of the smelting experiments, and in particular for the investigations of the system FeS—MnS. It is a well-known fact that pyrites (a native iron bisulphide of the formula FeS₂), when considerably heated, gives off a considerable amount of sulphur, and is converted into a product lower in sulphur. If, when this is being done, oxidation is prevented by the adoption of suitable measures (*e.g.* by heating in a Kryptol test-tube furnace or in a nitrogen atmosphere in the carbon-tube furnace), it is possible, as Friedrich² has already shown, to obtain, on heating to the melting point, an iron sulphide of constant composition FeS. Le Chatelier has already found that when pyrites is heated for a considerable time to about 1200° C., a product results whose composition corresponds to the formula FeS.

As initial material choice was made of pure crystals of

¹ *Revue de Métallurgie*, 1909.

² *Metallurgie*, 1908, No. II.

pyrites from Rio (Elba), the composition of which was found to be 46·80 per cent. iron and 53·12 per cent. sulphur, the theoretical formula FeS_2 being 46·55 per cent. iron and 53·45 per cent. sulphur. The pyrites, in fairly large pieces, was heated in a Tammann tube under nitrogen in the carbon-tube furnace. At red heat sulphur was given off in large quantities, and burnt in a long flame above the tube, thus ensuring the melt being free from oxygen. At the end of eight to ten minutes the contents were melted down to a very fluid mass, the sulphur having been liberated in lesser and lesser quantities, and finally ceased entirely.

The correct composition of the melt was tested by means of thermal and analytical checks. The fused reguli were perfectly compact and free from blisters, as well as hard and very brittle; fractured pieces were pronouncedly crystalline and very similar in colour to magnetic pyrites. The mean chemical composition was 63·28 per cent. iron and 36·70 per cent. sulphur, thus closely approaching the theoretical formula for FeS , with 63·52 per cent. iron and 36·40 per cent. sulphur.

It should be mentioned, also, that the melting tubes were not attacked at all, which is the reverse of Treitschke and Tammann's experience¹: the latter finding that iron sulphide quickly attacks porcelain and easily eats through the tube. Even when the times of melting were extended to half an hour or longer the inside of the tube was still smooth and snow-white. As already mentioned by Friedrich (*loc. cit.*), the rapid destruction of the melting tube may be attributed with certainty to a percentage of oxygen in the sulphide.

Manganese Sulphide.—For the purpose of making a pure manganese sulphide, the author began with green manganese sulphide.

As supplied, however, this contained a considerable percentage of manganese oxide and free sulphur, although found to be absolutely free from iron. The mean composition was as follows:—

	Per Cent.
MnS	82·0
Mn ₂ O ₄	12·5
Sulphur	5·0
Water	0·5

¹ *Zeitschrift für Anorganische Chemie*, vol. xlix, p. 320.

Since it is easy to convert Mn_3O_4 into MnS , when the former is rendered incandescent in a current of hydrogen, by the addition of sulphur, the commercial preparation containing oxygen was heated in a hydrogen current with the addition of an excess of sulphur, the following being the chemical composition subsequent to this treatment:—

	Per Cent.
MnS	96.58
Mn_3O_4	1.94
Sulphur	1.50

After repeating the operation, during which the temperature was raised to melting point, the final result was a sulphide in which the uncombined sulphur had entirely disappeared and the protoxide-content reduced to traces. In comparison with the initial material, which easily became partially slagged when melted down, the final preparation showed not the slightest signs of having attacked the melting tube, even when maintained at melting point for some time.

The reason of the absence of any mention in literature of any work on manganese sulphide, and especially on the system $\text{FeS} - \text{MnS}$, may perhaps be explained by the ease with which the commercial green manganese sulphide forms slag, and in view of the same discovery as to iron sulphide already made by Treitschke and Tammann.

REACTIONS FOR THE RECOGNITION OF SULPHIDE ENCLOSURES.

General reactions have already been elaborated for the purpose of recognising the sulphide enclosures because of their frequency and importance and on account of the ease with which they decompose under chemical influences, generally with a liberation of hydrogen sulphide. It may not be out of place here to give a critical *resumé* of the question.

The oldest information comes from Heyn and Bauer (*loc. cit.*), and mentions the possibility of showing, even without the aid of the microscope, places containing numerous sulphide enclosures.

Test-pieces were taken and roughly ground or smoothed with a smooth file, a silk rag placed over the pieces, and the

rag wetted with a solution of hydrochloric acid and mercuric chloride. A good formula for this is 10 grammes of mercuric chloride, 20 cubic centimetres of hydrochloric acid (1.124), and 100 cubic centimetres of water. If this is allowed to act for about five minutes it is sufficient in most cases. Where sulphide enclosures are present in the slide, H_2S is formed by the reaction of the hydrochloric acid, black mercuric sulphide being precipitated from the hydrochloric-mercuric chloride solution, which, adhering to the silk rag, permits of recognising the portions rich in sulphide.

This method is extremely convenient and reliable, and is specially suited for quickly and certainly discovering segregations in the material, since where sulphur-enrichments have occurred other segregation phenomena are usually present also.

The "sulphur prints" are coloured to a varying degree of intensity according to the distribution of the sulphide, and it is thus easy by their aid to discover the portions of a section from a somewhat large area which appear particularly adapted for the microscopical examination. In this connection, however, it is necessary to regrind the surface of the slip which has been exposed to the acid; otherwise when the microscopical observations are made, generally only black corroded holes will be visible in place of the sulphides. From its nature, however, the method does not appear suitable for determining very small detached enclosures in the form of sulphides observed under the microscope.

An absolutely similar procedure is known as Baumann's sulphur test. In this case a small piece of silver bromide paper, slightly wetted with dilute sulphuric acid, is brought into contact with the surface of the slide, the formation of sulphuretted hydrogen showing up the sulphide places by a local blackening of the silver bromide paper. Apart from the difficulty of manipulation, the process, of course, gives only reversed sulphur prints; moreover, when different silver bromide papers are used on the same sample the prints are often somewhat different, leading one to the supposition of a larger or smaller sulphur-content in the segregation, the reason for this being the varying percentage of silver in different papers.

Heyn and Bauer have already indicated a fundamental defect in the Baumann test. Owing to the dark colour of the silver phosphide it is not impossible in the case of samples containing phosphorus for spots to be caused in the silver bromide layer, both by sulphides and by phosphides, thus giving rise to erroneous conclusions. The mercuric chloride method has not this defect, since mercury phosphide does not appear dark coloured but only yellowish. Finally, the limitations mentioned for the mercuric chloride method apply equally for the Baumann test.

In order that the advantages of the characteristic sulphide reaction, based on the development of H_2S and on the secondary formation of a sulphide, may also be rendered accessible for the microscopical observation, it has been found advantageous to coat the slide direct with a layer of gelatine to which has been previously added a solution of cadmium salt or mercuric chloride rendered slightly acid. The H_2S liberated by the acid penetrates into the moist gelatine layer, and causes therein, above and in the immediate neighbourhood of the decomposing sulphide enclosure, a precipitation of the heavy metallic salt suspended in the gelatine. Care should be taken that the gelatine be as thick as possible, so as to be stiff enough to avoid its flowing off or shifting its position after being applied. The gelatine should be applied hot to the slide by means of a glass rod. This method permits of testing under the microscope, for its sulphidic nature, an enclosure placed in the microscope and observed therein, the stage being screwed back for the purpose of applying the gelatine, so that the place observed by the eye may be at once observed again in the microscope. Weak magnification has been found sufficient and practical for this purpose.

It may be well to mention here a reaction for sulphides given by Liesching¹ which appears suitable, in a given case, for imparting to the sulphide enclosures (which in themselves are often very shallow, and therefore very ill-adapted for photographic reproduction) a dark-brown colouring, which shows up in better relief from the surroundings. The slides are etched

¹ *Metallurgie*, 1910, p. 566, Dissertation.

for a brief period in picric acid (4 grammes of picric acid in 100 cubic centimetres of amyl alcohol), and subsequently in dilute nitric acid (4 cubic centimetres concentrated nitric acid in 100 cubic centimetres of amyl alcohol), being subsequently immersed for a short time in hot concentrated caustic soda solution. This operation imparts a dark-brown colouring to the sulphide enclosures.

REACTIONS FOR DISTINGUISHING BETWEEN FERROUS SULPHIDE AND MANGANESE SULPHIDE.

If non-metallic enclosures in a sample of steel have already been recognised as sulphides by one of the reactions previously mentioned, the far more difficult question of deciding whether the sulphur is combined with iron or manganese in the enclosures concerned arises. There are practically no investigations available for the purpose of deciding this question, and yet, from what has already been said, it is of extreme importance.

The difficulty of such differentiating reactions lies in the fact that the same combinations of two elements in close chemical relation to each other have to be dealt with; and it is at once apparent, therefore, that the chemical behaviour of these combinations will be very similar. Moreover, the combinations of the two elements, iron and manganese, occur as enclosures in considerable excess of the free element, so that when changes take place the combination and elementary iron or manganese often give the same reaction.

Thus no data on the question are to be found even in the above-mentioned papers dealing with the slag enclosures, Matwieff alone forming an exception. It is possible that yellowish-brown ferrous sulphide and dove-grey manganese sulphide are spoken of; this is true in so far as ferrous sulphide in fairly large flakes generally shows a yellowish-brown colour, while larger enclosures of manganese sulphide appear bluish-grey in incident light. It must, however, be stated that it may often be difficult even to a fairly trained eye to draw correct conclusions from the fallow colour, regarding the enclosures. It is very often difficult (if not quite impossible

in the case of small enclosures), especially in the case of manganese sulphide, to correctly recognise the tint. Thus, Law states (*loc. cit.*): "The sulphide occurring in steel varies very much in colour and composition. In some steels it is so pale in colour that it is difficult to photograph, whereas in others it is so dark that it may easily be mistaken for manganese silicate."

The only reaction, recognised in the literature, permitting of distinguishing between the two sulphides occurring in iron is contained in Matwieff's work already mentioned, dealing with the slag enclosures in wrought iron. According to this writer, ferrous sulphide is considerably darkened by tartaric acid, while manganese sulphide is not coloured.

There will now be given the results of a large series of etching experiments systematically carried out on sections with varying percentages of ferrous sulphide or manganese sulphide, or both together. The percentage of sulphide in the melts varied from a few tenths up to 10 per cent. Figs. 1 to 3, Plate II., show photomicrographs of such sections.

The prominence of the symmetrical arrangement of the crystalline grains of the iron (Fig. 2, Plate II.) is remarkable in connection with the higher percentages of iron sulphide. Manganese sulphide, on the other hand, is only visible in the form of numerous roundish spots in the ferrite, even with higher percentages of MnS (Fig. 1, Plate II.). It was, of course, natural to verify first of all the data given by Matwieff especially in view of other experimental conditions; and it was found in this connection that ferrous sulphide is indeed rendered considerably darker by etching with dilute tartaric acid, but that manganese sulphide also is darkened to a not inconsiderable extent even when an aqueous 1 per cent. solution of the tartaric acid acts on the slide in the cold state for a period of only 45 seconds, while Matwieff gives the duration of etching as 2 to 3 minutes for dilute tartaric acid in the cold. For the purpose of obtaining a good comparison, the procedure was carried on in such manner that only one half of the slide was etched; hence it was possible to observe simultaneously in the field of the microscope the etched portion of the

slide together with the non-etched portion for purposes of comparison.

One advantage of this method of etching is that the brownish or bluish-grey colour of the sulphides is rendered more plainly visible. When etching was done with a 2 to 3 per cent. solution (that is, a still considerably diluted solution) for a few minutes, as laid down by Matwieff, the sulphides were considerably corroded and partially eaten out.

Mention should be made here of Matwieff's experimental conditions, according to which there was no MnS whatever which had been liquid in the liquid iron bath. He drilled out a piece of puddled iron, and placed in the cavity the material to be incorporated with the iron (in this case the green manganese sulphide of commerce), together with some additional sulphur, after which he closed the cavity with an iron bung, and heated the bomb in a Méker furnace; the temperature attained in the oven being given as only $1300^{\circ} C$. The cylinders were then sawed through transversely, and afterwards polished. At a temperature of $1300^{\circ} C$. it is not possible, however, to fuse pure manganese sulphide. It is stated in the paper itself that the sulphide did not penetrate into the metallic iron. In addition to this there is the fact, as shown above, that commercial green manganese sulphide cannot be taken as pure manganese sulphide, since an artificial addition of sulphur must enhance the primary formation of ferrous sulphide in the iron tube.

Since tartaric acid has a great tendency to form easily soluble complex salts, it was interesting to try other organic acids for etching experiments. A large number were tried. Acids such as acetic, citric, oxalic, and picric, when applied in 1 per cent. aqueous solutions, all turned the ferrous sulphide brown in one minute; and the etching even acted upon the manganese sulphide, the latter also being turned considerably darker at the end of forty-five seconds. The action of picric acid was very favourable, attacking the sulphide in a very uniform manner.

In order to secure a finer degree of differentiation of the etching effect on the two sulphides, the organic acids were employed in solutions of various alcohols. Since it was pos-

sible to secure gradual control as to the degree of dissociation by this means, the result was a gradual toning down in the etching effect. It was found, for instance, that a 1 per cent. solution of acetic acid in ethyl alcohol turned the ferrous sulphide a brownish tint after three minutes' etching, while manganese sulphide was only rendered a very light blue. The ferrite was considerably roughened. This result would appear to correspond very nearly with Matweieff's statement for dilute aqueous solutions.

As a general rule it was found that 1 per cent. solutions of organic acids had the same effect on ferrous sulphide in about five minutes as 1 per cent. aqueous solution had in from forty-five seconds to one minute; manganese sulphide, on the other hand, remained considerably in the shade.

When experiments were carried further into the series of alcohols, it was found that in the case of amyl alcohol thirty minutes' etching was required to produce appreciable darkening of the ferrous sulphide, manganese sulphide remaining more tardy than ever. At the same time, however, it was found that the reaction on the ferrite was not restricted to nearly such a great extent by the alcoholic solution: a 2 per cent. tartaric acid solution in amyl alcohol, for instance, considerably attacking the ferrite, and colouring it with brownish spots after thirty minutes' etching. The etching effect on the sulphides should therefore not be too greatly retarded; in any case it is not advisable to make etchings with amyl alcohol and alcohols closely related thereto. One per cent. solutions of organic acids, particularly acetic acid and picric acid, in ethyl alcohol produced the best results.

It should be stated here that when the acid was prevented from acting too long and producing over-etching, a different behaviour of the metal surrounding the sulphide enclosures, especially the dark colouring or greater degree of corrosion, was not observed, and the sulphide enclosures appeared as though surrounded by haloes.

Only picric acid behaves in a specially noteworthy manner, inasmuch as after a few minutes' etching extremely delicate, characteristically undulating veins occur in the ferrite, these veins connecting the individual ferrous sulphide enclosures,

and hence splitting up the ferrite crystals into smaller ones (Fig. 4, Plate II.).

Moreover, picric acid etches in a steady uniform manner, and does not eat out the sulphide; it, however, strongly attacks the ferrite, rendering it distinctly rough. The occurrence of the characteristically undulated veins connecting the individual enclosures was not observed in the case of manganese sulphide.

Le Chatelier, writing on the same observation, states:—

“Nous avons cependant observé que lorsque l'on fait une attaque par un réactif approprié, par exemple avec l'excellent réactif indiqué par M. Igevsy, solution à 5 p. 100 d'acide picrique dans l'alcool absolu, les parties du fer voisines du sulfure se corrodent plus rapidement, comme si elles étaient moins pures. . . . Il semble donc qu'au voisinage immédiat du sulfure, et suivant certaines lignes joignant les taches de sulfure, le métal jouisse de propriétés particulières.”

This etching phenomenon may be very simply explained by the fact that along those fine lines extremely delicate films of ferrous sulphide extend between the individual ferrite grains as the finest offshoots of the more massy sulphide separations. Picric acid, which considerably roughens the ferrite, naturally takes, mechanically, a line of least resistance along the limiting surfaces between sulphide enclosure and ferrite crystal.

Particular stress should be laid on the fact that among the organic acids in alcoholic solution picric acid really darkens the sulphide in a very uniform manner, and shows less tendency than other acids partially to corrode the sulphide. Free inorganic acids, even when in a solution of alcohol, act too energetically on the sulphides, although the time of etching may be very short.

The experiments were also extended to salts of organic acids, the effect being similar to that produced by the free acids. As a general rule, the dilute salt solution produced nearly the same etching effect as the free acid in ethyl alcohol. Thus, with a 2 per cent. aqueous solution of sodium acetate and an etching duration of one minute, it was observed that ferrous sulphide was darkened to a brownish tint, while manganese sulphide remained very light.

The attack on the ferrite was notably slight. Neutral potassium oxalate in a 1 per cent. aqueous solution also produced darkening of the ferrous sulphide more rapidly and to a greater degree. Other salts of organic acids behaved in a similar manner.

Experiments based on typical iron and manganese reactions (for example, the employment of a coating of gelatine containing an acidulated solution of potassium ferricyanide) failed, since although the sulphides, owing to the ease with which they decompose, reacted at once, the result was obscured by the surrounding metal, which also reacts, although to a considerably lesser degree. When the slide was coated with gelatine containing some solution of potassium ferricyanide and hydrochloric acid, the places rich in ferrous sulphide were immediately coloured deep blue, being shown up in great relief against the sulphide-free portions, and being observable with the naked eye. This reaction seems to be not unsuited for discovering segregations in the material which have generally a considerably lower chemical resistance; it is therefore mentioned here.

While the etching effects previously described are based on a chemical attack of the sulphides, a series of experiments will now be mentioned in which the behaviour of the sulphide enclosures was observed when a coating was formed on the slides. Provided it were possible to form a coating on the slide which will be produced more rapidly on one sulphide than on the other, it would thus be possible to differentiate between the two sulphides.

It seems interesting to observe the behaviour of the sulphides on tempering, that is, on heating in a jet of air, which caused the slide to be coated with a fine oxide film, and this film was coloured according to its thickness. The temper colours of iron, as is well known, pass through dark yellow, brown, red, violet and blue to grey. For the purposes of tempering, the slide, polished side upwards, was laid on a thin sheet of iron, and the latter heated by a Bunsen burner: the temper colours being observed by reflected light. As soon as the desired colour was attained the slide was quickly removed with the tongs and rapidly cooled by floating it upon cold water

or mercury. With a view to preventing any irregularities, care should be taken to see that the tempered surface of the slide is not wetted during the above operation. This is obviated by using mercury for cooling, but the mercury does not cool the slide nearly so quickly, being, however, preferable to water for small slides or for brittle, cracked material.

When the sections were tempered in the polished state only, irregularities showed themselves both in the tinting of the ferrite and of the sulphides. Very good results were, however, observed when the slides were etched for quite a short time with dilute solutions of organic acids prior to being tempered in the manner mentioned above. It was found most advantageous to temper the ferrite to dark yellow, the ferrous sulphide assuming a beautiful dark blue colour on a bright yellow ground. When a Nernst lamp was used for this observation in place of very favourable daylight illumination, the ferrous sulphide was found to appear reddish-violet. A slide treated in the manner mentioned shows up to really excellent effect in the microscope, especially when the sulphide-content is somewhat high; manganese sulphide, on the contrary, appears dull grey to brightish-white after tempering.

The contrast can often be enhanced by the use of colour filters, blue and green filters being specially advantageous. The green filters show ferrous sulphide as deep blackish-green on a yellow ground, and manganese sulphide as light green on a darker ground.

The more favourable an etching is for the sulphides as regards the proportions of darkening, the more favourable will it act as a preliminary etching for tempering. It may here be repeated that as a general rule 1 per cent. solutions of organic acids in ethyl alcohol yield the best results; and when it was stated that, among the organic acids, picric acid in particular gives very uniform etching, it might have been said this acid is worthy of special consideration for the etching-tempering also.

Photomicrographs 5 and 6, Plate II., show photographs of ferrous sulphide and manganese sulphide respectively, taken with a colour-sensitive plate and yellow screen in accordance with the temper method just described. The difference even

here is very obvious, although the colours only appear, of course, according to their relative brightness.

It may not be uninteresting to mention that Oberhoffer¹ has successfully employed the same temper method, together with preliminary etching with picric acid, especially for the purpose of discovering iron phosphide. He tempers the weakly-etched slide to a blue colour, iron carbide being coloured orange-red, and ferrite, blue, while the iron phosphide assumes white to yellowish tints. But he did not etch with organic acid in general and picric acid in particular, and afterwards temper for discovering the nature of the sulphide enclosures. The iron used by Oberhoffer contained 0.3 per cent. manganese and 0.04 per cent. sulphur.

Wüst states² in connection with investigations on the influence of sulphur in pig iron, that on etching and tempering the sample from yellow to the red colour of the cementite, in accordance with Oberhoffer's method, the crystals rich in sulphur remain white, or, at the most, assume a light grey colouring. In connection with this, Wüst remarks that as regards the nature of these light crystals it is only possible to say that they are rich in sulphur, as determined by Baumann's test. Wüst apparently knew nothing of the different behaviour of the two sulphides.

On the occasion of some etching experiments using mercuric chloride as a salt of extremely low dissociation in an aqueous solution, it was observed that the sulphide enclosures became covered with a quantity of fine mercury drops, which lay thickly, especially on the ferrous sulphide, completely covering it over. On carefully polishing the slide with a soft cloth, thereby removing the mercury drops, the iron sulphide appeared considerably corroded, while the manganese sulphide was uncorroded.

This reduction phenomena observed with mercuric chloride led to the experiments being continued with the salts of precious metals; but it has also been found by metallurgical chemists that the natural sulphides have a strong reducing action on gold chloride.³ Thus it was shown that on

¹ *Metallurgie*, 1908, p. 19.

² *Ibid.*, 1908, p. 447.

³ Meunier, *Compt. Rend.*, 84, p. 638 [1877]; Leo, *Die Anlauffarben zur Untersuchung opaker Erze*, Diss., Dresden.

immersion for a short time in a 3 per cent. solution of boiling silver nitrate, the ferrous sulphide was coloured a beautiful uniform violet-blue, and in this state, of course, it was very hard to distinguish it from the dove-grey, slightly darkened manganese sulphide when daylight illumination was used. On slightly repolishing the slide with a soft cloth, however, and observing it in strong artificial light (such as the light from a Nernst lamp), the ferrous sulphide appeared reddish-violet, and the manganese sulphide blue-grey. The difference is, of course, not very marked, though definitely and regularly recurrent. The reason for the phenomena is that in the case of ferrous sulphide the yellowish ground shimmering through changes the hue, while in the case of manganese sulphide the natural blue-grey colour is intensified by the deposit.

Gold salt solutions produce, on the sulphides, considerable precipitation of a fine gold deposit of a warm brown colour. It is therefore unsuitable for distinguishing between the sulphides. It should, however, be mentioned that in the case of meltings rich in ferrous sulphide, a sharply defined border of ferrite (turned brown) formed around the sulphide, this border being of great uniformity as regards colour and extension. This precipitation of the gold may be traced to local electrolytic reaction between sulphide and adjacent iron. Manganese sulphide, which precipitates the gold more slowly, apparently did not produce this phenomena. The gold precipitated adhered very firmly to the slides.

On glancing again at the reactions which have been described for distinguishing between the sulphides, it is found: That 1 per cent. solutions of organic acids in ethyl alcohol, with five minutes' etching, produced considerable darkening of the ferrous sulphide as compared with the manganese sulphide. After a short preliminary etching with alcoholic solutions of organic acids (preferably picric acid), the successive tempering to dark yellow leaves the ferrous sulphide blue and the manganese sulphide a dull whitish. This reaction appears to be well adapted for distinguishing between the sulphides. It was practically exclusively employed in the following experiments also.

EXAMINATION OF THE SYSTEM $\text{FeS} - \text{MnS}$.

During the tempering experiments described above, observations were made which led to the supposition that mutual solubility exists between the two sulphides, even in the solid condition, at definite concentration. In order to gain more exact knowledge of these conditions (which promised important conclusions concerning the constitution of the sulphide enclosures in iron) it seemed of importance, first of all, to investigate the system $\text{FeS} - \text{MnS}$ more thoroughly, especially as nothing definite has been established in the literature dealing with the matter; the most contrary opinions seem rather to be found in the case of individual investigators.

It has been already mentioned that, in Law's opinion, solid solutions of both sulphides are possibly to be suspected in the sulphide enclosures of iron (p. 41; *cf.* also p. 69). Wüst¹ states: "Even if by the presence of manganese a portion of the latter is combined with the sulphur, nothing will be altered in the mode of appearance of the sulphur. Possibly the light small crystals then consist of mixed crystals of ferrous sulphide and manganese sulphide." Both authors thus assumed that an uninterrupted series of solid solutions exists between the two components, ferrous sulphide and manganese sulphide.

According to Schenk,² in the case of the alloys the relations between the two sulphides are generally quite simple. Meltings miscible in all proportions, on solidifying allow the components to crystallise out in the pure state. Reference is also made in this connection to Le Chatelier's observations.³ He found that in the mixture of iron, manganese, and sulphur, the manganese did not combine with all the sulphur, but that FeS could also be found. He found yellow ferrous sulphide in the form of spheres, with crystals of manganese sulphide in the middle; or even crystals of manganese sulphide and spheres of yellow ferrous sulphide, detached and side by side. According to these two experimenters, the existence even of a quite limited degree of solubility in the solid condition between the two sulphides was contested. There is thus some obscurity concerning the true nature of the sulphide enclosures.

¹ *Metallurgie*, 1908, p. 447.
C.S.M. (1912)

² *Physikalische Chemie der Metalle*.

³ *Loc. cit.*
D

Full mention has already been made concerning the original materials of the components, ferrous sulphide and manganese sulphide. A few details will, however, be given concerning the instrument used for making the critical point determinations. A thermocouple of platinum and platinum-rhodium wire was employed for measuring the temperature. Since the wire of the couple was only 0.2 millimetre in diameter, it was possible to use narrow thin-walled shielding and insulating tubes, so that the couple itself reacted very well to small thermal effects. The measuring instrument employed was a Siemens-Halske voltmeter having a range up to 1600°C . Since very high temperatures were sometimes necessary, the melts were carried out in a carbon tube furnace, concerning which details have already been given on p. 33.

It may be permissible at this stage first of all to say a few words regarding the melting-points of the pure components of the system.

A quantity of data is available relating to the melting-point of pure ferrous sulphide, these data for the most part being in good agreement. Le Chatelier found for a product having the approximate composition FeS , a melting-point of 1200°C . Friedrich¹ gives 1171°C . for pure ferrous sulphide, K. Bornemann² 1194°C ., and W. Biltz³ $1197^{\circ}\pm 2^{\circ}\text{C}$. The author found a mean melting-point of 1188°C . in the carbon tube furnace under nitrogen, this result being very close to those found by Bornemann and Biltz.

As regards the melting-point of manganese sulphide, on the other hand, very varying statements are to be found in the literature, the values fluctuating between 1200° and 1600°C .

Le Chatelier⁴ states: "Le sulfure de manganèse, ayant pris une symétrie cristalline, est nécessairement l'élément de première consolidation, c'est-à-dire que son point de fusion est supérieur à celui du manganèse et par suite du fer; il est donc très éloigné de celui du sulfure de fer."

The melting-point of the iron was found to be 1510°C .

Arnold⁵ states: "Dove-grey manganese sulphide only melts at white or yellow heat. . . ."

¹ *Loc. cit.*

³ *Zeitschrift für Anorg. Chemie*, 1908, p. 272.

² *Metallurgie*, 1908, p. 64.

⁴ *Loc. cit.*

⁵ *Loc. cit.*

On the other hand, Law¹ states: "The author has been unable to verify this statement [made by Le Chatelier, that manganese sulphide has a higher melting-point than iron], and has had no difficulty in melting manganese sulphide in an ordinary coke-fired assay furnace, which was quite incapable of melting mild steel."

Wüst² writes: "We know that the sulphur in pig iron containing manganese becomes insoluble as MnS in the metal bath, and endeavours to separate itself"; and further: "The good development of the crystals [of the sulphide] points to the fact that they were not prevented in the endeavour to crystallise, and thus they existed while the remaining mass was still fluid." On the other hand, Wüst has confirmed the fact that in the case of material more poor in carbon the portions rich in sulphur crystallise only after the bulk of the remaining mass of metal has solidified.

Melting experiments made by the author with the manganese sulphide described on p. 36 gave the melting-point as 1550°C . This product, however, contained a good deal of oxygen. The preparation when weakly roasted in sulphur in a jet of hydrogen was only with difficulty melted in the carbon tube furnace; the melting-point was found to be 1620°C ., being thus some 70° higher than in the case of the initial material containing oxygen. The fused material did not attack the melting tube of the best refractory material, while the initial preparation, containing protoxide, easily slagged the surface of the tube. Fig. 15, Plate IV., shows a photomicrograph of the pure manganese sulphide as re-melted under nitrogen.

The following table contains the composition of the individual melts and the recorded critical points:—

¹ *Loc. cit.*

² *Metallurgie*, 1908, p. 447.

TABLE I.

No.	Result of Analysis.		Critical Points.		Remarks.
	FeS.	MnS.	I.	II.	
	Per Cent.	Per Cent.	° C.	° C.	
1	100.00	...	1188
2	96.80	3.15	1185
3	95.30	4.67	1182.5
4	93.05	6.98	1182	...	Eutectic composition—Fig. 7, Plate III.
5	91.47	8.62	1185.5	...	Fig. 8, Plate III.
6	88.08	11.82	1211.5	1181
7	84.70	15.23	1237	1181	Fig. 9, ..
8	80.89	19.06	1261	1181
9	75.09	24.87	1288	...	Fig. 10, ..
10	72.26	27.72	1312	...	Fig. 11, ..
11	66.56	33.38	1327	...	Fig. 12, ..
12	65.55	34.59	1341.5
13	59.79	40.17	1362	...	Compound $\text{Fe}_3\text{Mn}_2\text{S}_5$ —Fig. 13, Plate IV.
14	51.77	48.14	1418
15	41.08	58.89	1463
16	29.21	70.82	1510	...	Fig. 14, Plate IV.
17	21.13	78.80	1548
18	10.45	89.65	1585
19	...	100.00	1620	...	Fig. 15, ..

THE THERMAL DIAGRAM AND THE MICROGRAPHIC RESULTS.

The above tabulated data combined into a diagram give the curves shown in Fig. 1.

From the point *a* (the melting-point of the pure ferrous sulphide) a lowering of the melting-point, even though slight, first takes place on account of the low percentage of manganese sulphide. The minimum, with 1181°C ., is at about 7 per cent. The resultant eutectic is thus formed of 93 per cent. FeS and only 7 per cent. MnS. From this point onwards there is a steady rise in the melting-point, which at point *f* (the pure MnS), the value of 1620°C . is finally attained. The second critical point corresponding to the eutectic could not be determined thermally in the case of the hypo-eutectic melts on account of its close proximity to the first critical point, as the heat effects in the case of the sulphides are in no wise very considerable. In the hyper-eutectic melts also the second critical point, which at the commencement is very definite, is soon no longer perceptible. Further light is thrown on this fact by the microscopical results.

The sections were prepared for the microscopical examination in the manner previously described, that is, by means of etching-tempering; a preliminary etching of about 30 seconds' duration in alcoholised picric acid was given, the sections being afterwards placed on a sheet of iron and tempered over a Bunsen burner. The melts rich in ferrous sulphide were tempered to a decided blue, but the melts rich in manganese sulphide took a considerable time to attain a light speiss-

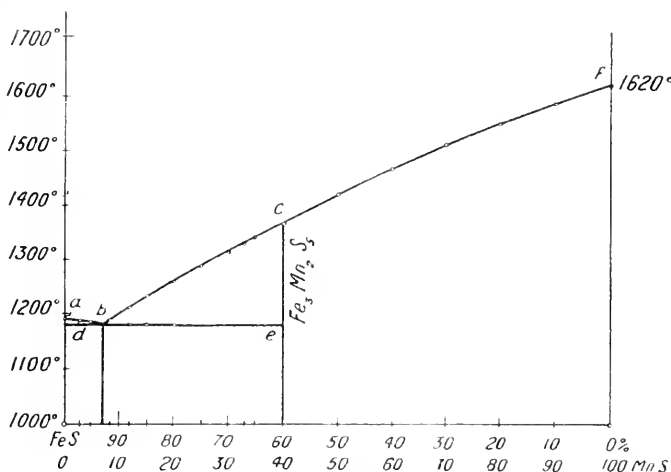


FIG. 1.—System FeS—MnS. (See Table I.)

yellow temper colour. The quenching was carried out in mercury.

The microscopic examination showed, with 7 per cent. MnS, uniformly dark blue coloured areas in the extremely brittle, crumbly slides, small, uniformly distributed light points occurring in these areas (Fig. 7, Plate III.). Increase in the percentage of manganese sulphide caused the appearance of bright yellow substances between the dark eutectic areas, these substances taking the appearance of crystal skeletons allowing more and more support to the crumbling brittle eutectic, so that the melts are more easily ground, while the hypo-eutectic melts crumble away in the fingers. The light yellow crystals increase rapidly with in-

creasing percentage of manganese sulphide, and grow, especially in length, as a result of which the dark blue tempered eutectic appears in long linear layers intersecting at an acute angle in accordance with the crystallisation angles of the light yellow type of crystal (Figs. 10, 11, 12, Plate III.).

With 30 to 35 per cent. manganese sulphide the light crystal type takes up nearly the entire area, and with 39 per cent. MnS the last portions of the eutectic, *i.e.* of the free ferrous sulphide, are only to be found between large areas which appear coloured a uniform light yellow (Fig. 13, Plate IV.). At 40 per cent. even these portions disappear, and only uniformly light-yellow tempered areas occur, with not a trace of ferrous sulphide (Fig. 14, Plate IV.).

These micrographical results, taken in connection with the thermal diagram, give evidence of the apparently not unimportant fact that at about 60 per cent. of ferrous sulphide a chemical combination takes place between the two components FeS and MnS , to which accordingly is given the formula 3FeS , 2MnS , or $\text{Fe}_3\text{Mn}_2\text{S}_5$, and which melts at 1365°C . If the percentage of ferrous sulphide in these melts is higher than indicated in the formula, a eutectic of FeS and the compound $\text{Fe}_3\text{Mn}_2\text{S}_5$, of freezing-point 1181°C . is formed.

On the other hand, unlimited solubility exists between the compound and, say, an excess of MnS even in the solid state present in the melts. A continuous series of mixed crystals accordingly exist between the combination $\text{Fe}_3\text{Mn}_2\text{S}_5$ and the final member MnS , these mixed crystals differing thermally from each other in the fact that their freezing-point is always shifting higher, reaching and exceeding with a percentage of 30 per cent. FeS the freezing-point of pure iron. The appearance of the photomicrographs of melts above the combination $\text{Fe}_3\text{Mn}_2\text{S}_5$ no longer changes (Figs. 14 and 15, Plate IV.).

The diagram of the system $\text{FeS} - \text{MnS}$ falls into two simple systems—the first between FeS and a compound $\text{Fe}_3\text{Mn}_2\text{S}_5$ with 60.25 per cent. FeS and 39.75 per cent. MnS , or

	Per Cent.
Iron	38.27
Manganese	25.10
Sulphur	36.63

and the second between this compound and pure MnS. In the first system the solidification of MnS takes place along the curve *ab* (Fig. 1), and that of the compound $\text{Fe}_3\text{Mn}_2\text{S}_5$ along *bc*; *dbe* shows the freezing of the eutectic; everything is liquid above *abe*, and everything solid below *dbe*. In the second system the mixed crystals commenced to separate as shown in curve *cf*, everything above *cf* being liquid (liquidus curve). It was not possible to plot the solidus curve thermally with any degree of certainty, and it is therefore not given.

The outlines of the curves of the two individual systems connect without any appreciable kink, so that it is not possible to see at once from the thermal curve alone the occurrence of the compound $\text{Fe}_3\text{Mn}_2\text{S}_5$ and the series of mixed crystals above it, since the critical point of the eutectic which would hold theoretically for up to about 40 per cent. MnS eluded record considerably earlier on account of the slight heating effect.

In the molten and slowly solidified condition, the pure iron sulphide is extremely brittle and crumbly, being broken up into small granules when lightly pressed between the fingers. Additions of up to 7 per cent. of manganese sulphide do not change this property in any way, and hence such melts can only be polished in very small pieces after due precautions have been taken. The pieces were carefully embedded in a mixture of gypsum and steatite, and ground after hardening in this envelope.

Similarly, the ferrous sulphide in iron is an extremely brittle substance, so that, in spite of careful grinding, the sulphide is easily forced out of the section, leaving behind large black holes, and thus imparting a very unsightly appearance (*cf.* Figs. 1 and 2, Plate II.).

If with higher manganese sulphide contents the melts are composed only of mixed crystals, the physical qualities are accordingly entirely changed. The melts are very firm and hard, and are broken only with difficulty. This property is most pronounced in melts of from 70 to 90 per cent. manganese sulphide. The melts containing from 7 to 40 per cent. manganese sulphide form the transition from the brittle material

to the tenacious material of the combination $\text{Fe}_3\text{Mn}_2\text{S}_5$ and of the mixed crystals, since in them the crystal skeleton of the primarily separated compound $\text{Fe}_3\text{Mn}_2\text{S}_5$ forms a celliform enclosure round the brittle eutectic, and offers it support much the same as the skeleton does to the animal body. In the neighbourhood of the combination $\text{Fe}_3\text{Mn}_2\text{S}_5$ the melts are characterised by a great tendency to crystallisation: beautiful arborescent crystal skeletons of up to 6 millimetres and more being found in the pipe.

THE INFLUENCE OF MANGANESE SULPHIDE ON THE BINARY EUTECTIC $\text{Fe} - \text{FeS}$.

Before we are able to derive, from the above study of the binary system $\text{FeS} - \text{MnS}$, precise conclusions as to the constitution of sulphide enclosures in iron and steel, it should be

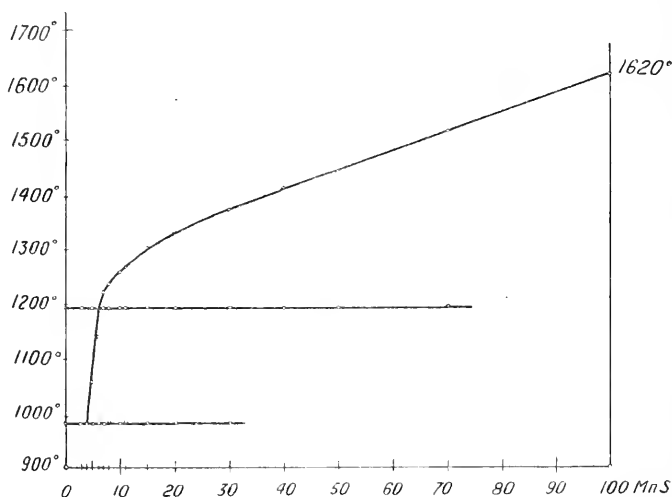


FIG. 2. (See Table II.)

considered that according to Treitschke and Tammann,¹ and Friedrich,² the ferrous sulphide in iron is present in the eutectic mixture with iron; but this eutectic is so infinitely fine that it is not possible to resolve it into its constituents

¹ *Loc. cit.*

² *Loc. cit.*

when cooled normally, even when high magnification is employed.

We are therefore faced with the fresh question: How does manganese sulphide (concerning which the preceding investigations have shown that it forms, with ferrous sulphide, a combination of favourable properties, and also mixed crystals) behave in relation to the eutectic $\text{Fe} - \text{FeS}$ present in the bath, *i.e.* in the large iron-excess?

First let us say a few words on the binary systems $\text{Fe} - \text{FeS}$ and $\text{MnS} - \text{Fe}$. For an exhaustive study of the question reference must be made to the above-mentioned papers of Treitschke and Tammann, and of Friedrich. It would be sufficient to say here that according to Friedrich's data the diagram takes a considerably simpler form. He is of opinion that the occurrence of various thermal effects in the case of the investigators first named, is attributable to an impurity which might very well exist in an oxygen combination of the iron, the considerable corrosion of the melting tube also favouring this theory. At all events it is obvious from both diagrams that the iron sulphide enclosures deposited in iron and steel consist of a eutectic with about 15 per cent. of iron and 85 per cent. of ferrous sulphide, which does not freeze before 980°C . Hence there is no pure ferrous sulphide in these enclosures, but a ferruginous eutectic melting at 200° lower.

No accurate data can be found in the literature with reference to the iron-manganese sulphide system. If, however, a eutectic did exist between both components, then, in the pure iron, the enclosures of the manganese sulphide would, as the last freezing constituent, be forced into the interstices of the ferrite grains, and give on the polished section a similar network to that given by FeS . This, however, is never the case. On the other hand, the presence of fields of mixed crystals is excluded, since even when the slightest additions of manganese sulphide are made to the iron bath, diminutive roundish enclosures of manganese sulphide show themselves in the polished section—a fact to which Le Chatelier has already referred.

It may on the contrary be assumed that the manganese sulphide already in a liquid condition is not miscible with

the liquid iron bath, and, like drops of oil in water, float about at first liquidly in the iron bath, in the form of spherical products, and endeavour to separate according to specific gravity. On the temperature of the bath falling, these drops freeze, and finally the particles suspended in the melt in the form of fine, solidified globules are held back by the freezing ferrite grains and their egress prevented.

This view has also received other support. Thus, Wüst states¹ in a study on the influence of segregation on the strength of mild steel: "Unfortunately the behaviour of the sulphur in the liquid solution and on the freezing of iron alloys is at present not clearly recognised, though it appears very probable that there is a separation of sulphides even in the liquid state."

For the purpose of investigating the influence of manganese sulphide on the eutectic $\text{FeS} - \text{Fe}$, a commencement was first of all made on an alloy containing 25 per cent. iron and 75 per cent. ferrous sulphide, which thus contained, together with the eutectic of both components, an approximately 10 per cent. iron-excess. To this alloy, of always uniform composition, increasing quantities of manganese sulphide were added, and successive determinations of critical point and microscopical examination of the melts carried out.

We might imagine this series of investigations as a portion of an examination of the ternary system $\text{Fe} - \text{FeS} - \text{MnS}$; and in this case the series of melts would rest on the thick line DB in the triangle ABC (Fig. 3). The author, however, whose object was the investigation of the constitution of the sulphide enclosures deposited in the large excess of iron, did not pursue further the investigations concerning the ternary system, inasmuch as they were not within the scope of the present work.

The author gives also a graphical representation of the critical points tabulated on p. 60, in which the eutectic initial melt $\text{Fe} - \text{FeS}$ was, as it were, conceived as being a component of a binary system. This was done for comparison with the curve of the binary system $\text{FeS} - \text{MnS}$.

For the purposes of the melts, the three components, ferrous

¹ *Metallurgie*, 1910, p. 369.

sulphide, manganese sulphide, and finely filed electrolytic iron, carefully and thoroughly mixed, were melted down in a short-circuited furnace in an atmosphere of nitrogen. Immediately before taking the cooling curves, care was taken to see that the mass was well stirred up, since when kept for some time in the molten state the melts showed great tendency to segregate, the natural result of which would have been to impair the critical point determination. It was possible after a little practice to attain homogeneous results.

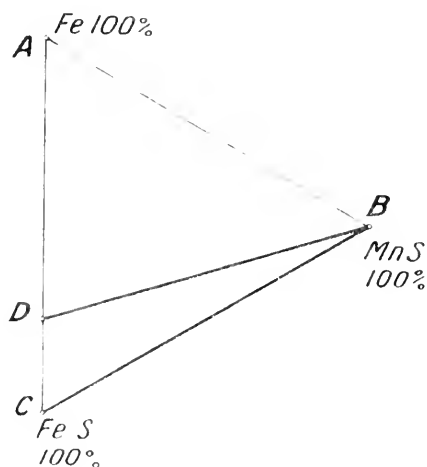


FIG. 3.

Table II. (p. 60) contains the compositions of the melts, arranged in order of increasing MnS-content; also the recorded critical points.

Critical point I. shows the freezing of the iron-excess. Critical point II. corresponds (above all in MnS-free melts) to the generation of heat on the freezing of the eutectic Fe-FeS. Both critical points are in perfect agreement with Friedrich's diagram. The position of the eutectic critical point was not markedly influenced nor lowered by an increasing MnS-content, but it showed, on the other hand, a tendency to raise its position by 10° to 15° C. This behaviour was explained by a slight tendency to under-cooling, which was compensated by the MnS-con-

tent, which might, so to speak, be set down to an inoculative or germinal effect.

TABLE II.

No.	MnS.	Critical Points.			Remarks.
		I.	II.	III.	
	Per Cent.	° C.	° C.	° C.	
1	0	1194	980	...	Fig. 16, Plate IV.
2	3	1192	980	...	Fig. 17, „
3	5	1193	995	1058
4	6	1194	980	1140
5	7	1193	985	1224	Fig. 18, „
6	8	1193	995	1235
7	10	1192	980	1253	Figs. 19 and 20, Plate V.
8	11	1193	990	1266
9	15	1193	985	1302	Fig. 21, „
10	20	1192	983	1333
11	30	1193	984	1370	Fig. 22, „
12	40	1193	...	1409
13	50	1193	...	1440
14	70	1193	...	1515	Fig. 23, „

The third and most important series of critical points does not commence until about 5 per cent. MnS. Up to a MnS-content of 20 per cent. it is not easy to determine on account of the small heating effects. The position of this series was determined by repeating the individual melt a number of times. In addition to the critical points given in the table, further weak heating effects were regularly confirmed in the melts at the following temperatures, viz. 1301°, 1152°, 1089°, and 1032° C. These critical points, however, occurred quite independently of a higher or lower MnS-content. They were most pronouncedly noticeable in melts free from manganese sulphide. Even when the mutual ratio between Fe and FeS was intentionally altered, the critical points did not shift their positions. They may be attributed to an influence of slight quantities of residual hydrogen gas in the electrolytic iron. This supposition is also supported by the fact that these critical points entirely disappeared on repeatedly re-melting the same melts. It may be mentioned that A. Müller¹ also

¹ *Über die Darstellung des Elektrolyteisens, dessen Zusammensetzung und thermische Eigenschaften* (Dissertation).

noticed a similar behaviour in pure electrolytic iron. The values in the above table are combined to form a curve (see Fig. 2).

MICROSCOPICAL RESULTS.

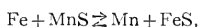
The melts were ground and submitted to microscopical examination after the etching-tempering. It was found most practical for developing the structure, to give a brief preliminary etching of 30 seconds with organic acid, preferably alcoholic picric acid, with subsequent tempering to yellow. Melts with up to 4 per cent. manganese sulphide show only a ground mass which is indistinguishable in colour from the pure Fe-FeS-eutectic; and in this ground-mass only the excess metallic iron appeared to be deposited in roundish spots arranged as crystal skeletons (Fig. 17, Plate IV.). Not a trace of the manganese sulphide was to be seen. A more accurate comparison of these sulphide melts containing very little manganese sulphide, with those of the MnS-free initial alloy Fe-FeS. produces, however, some striking differences.

The initial alloy, melted under the same conditions and cooled, shows in a very beautiful manner the characteristic feathery structure of the Fe-FeS-eutectic, such as is shown by the larger melts in the neighbourhood of the eutectic composition, 15 parts iron plus 85 parts ferrous sulphide, and which have already been recognised by Le Chatelier and Friedrich (Fig. 16, Plate IV.). The illustration shows, moreover, the primarily frozen, large light iron crystals, while the finer eutectic iron enclosures are generally on grinding pulled out of the brittle sulphide mass, leaving black holes behind. Quite different is the aspect of the melts containing a low proportion of MnS; these show, together with the primary iron enclosures, only a uniform ground-mass, the fine marking of the Fe-FeS-eutectic having entirely disappeared in spite of equally slow cooling. It must be added that the sulphide mass has become still more brittle and crumbly, and is much more liable to crumbling when grinding than are melts of the binary eutectic Fe-FeS, as may be seen from the

photographs of sections 17–21, Plates IV. and V. On these photomicrographs, the primary large iron crystals appear mostly dark to black, since in all probability they were tempered a deep orange yellow to luminous red. However, this remark is only made *en passant*.

Although it was not possible to produce direct thermal and microscopical proof of a ternary eutectic Fe – FeS – MnS from this single series of melts, yet the author felt justified in assuming a ternary eutectic, according to the above observation, whose freezing-point underwent no appreciable lowering by the small MnS-content, so that in the observations it practically coincides with that of the binary eutectic Fe – FeS; and it was not possible to split up the extremely fine structure into its individual constituents under the microscope even with high resolving power, though it was often possible to do this in the case of the Fe – FeS-eutectic.

Since the formation of a ternary eutectic because of the low MnS-content appeared less important for the influence of the manganese sulphide on the binary eutectic Fe – FeS, this question was not carried further, and only a complete investigation of the ternary system can finally settle the point, which would be quite out of the scope of the present work. In addition, with a larger excess of iron and but little ferrous sulphide, a reaction of the iron on the manganese sulphide will take place, with the re-formation of FeS and Mn according to the equation



to which we shall revert later on. We should then, however, have a quaternary system of the components Fe, Mn, FeS, and MnS, a check not being possible on the proportions of the individual components.

The most important feature, at all events for the present study, is that this eutectic is very brittle and crumbly, and does not freeze before 980° C.

If now the MnS-content in the melt rises above 4 per cent., a primary crystal type occurs in the sulphide eutectic, and remains a faded whitish colour when etched, the whole

appearance of this crystal type also, reminding one of the crystals of the combination $\text{Fe}_3\text{Mn}_2\text{S}_5$ found in the system $\text{FeS} - \text{MnS}$. As in that case, the orientation of these bright crystals is the same in the present instance also, and the present crystals are, in particular, considerably softer than the eutectic surrounding them, as Fig. 21, Plate V. (15 per cent. MnS) plainly and beautifully shows. This primarily formed crystalline type increases rapidly in area, exactly as in the binary system $\text{FeS} - \text{MnS}$, imprinting its favourable qualities on the molten regulus in an increasingly marked manner, so that the melts, in consequence of a fair amount of tenacity, can only with greater difficulty be splintered by striking, and can be much more easily worked when grinding, since they do not crumble up under the hand on the grinding disc as the brittle iron sulphide does.

With 30 per cent. manganese sulphide these crystals take up practically the whole area, restricting the sulphide eutectic to islets where the primary iron layers are mostly concentrated. Before 40 per cent. manganese sulphide has been attained the eutectic disappears completely, and the iron enclosures decrease more and more, corresponding to the smaller share of the initial alloy, so that the eye always encounters a uniform, bright area in the microscope, which does not darken even by very protracted tempering.

A glance at Table II. (p. 60) will show that the third critical point occurs in coincidence with the appearance of the bright primary crystals in the eutectic at about 5 per cent.: this critical point going upwards steeply (see curve, Fig. 2), and soon assuming the form of the curve applicable in the system $\text{FeS} - \text{MnS}$ to the crystals of the combination $\text{Fe}_3\text{Mn}_2\text{S}_5$, and to the mixed crystals of this combination with MnS which lie above the former. In making this comparison it should be considered that the MnS -content in Table II. and in the diagram (Fig. 2) respectively refer to the percentage proportion of MnS in the total composition. If the MnS -contents are reduced to the percentage quota of the total ($\text{MnS} + \text{FeS}$), and are contrasted with the corresponding compositions in the binary system, the following table is obtained:—

TABLE III.

Per Cent. of Manganese Sulphide.	Per Cent. of Manganese Sulphide in (FeS + MnS).	Recorded Critical Point.	Critical Point in System FeS - MnS.	Difference.
		° C.	° C.	° C.
7	8	1220	1190	+30
10	13	1250	1220	+30
15	19	1300	1260	+40
20	25	1330	1290	+40
30	36.5	1370	1350	+20
40	47	1410	1400	+10
50	57.1	1445	1450	- 5
60	66.7	1480	1485	- 5
70	75.7	1520	1530	-10
80	84.2	1550	1560	-10
90	92.3	1590	1590	± 0

Thus, when the critical point, after rising between 4 and 7 per cent., has proximated to that of the system FeS - MnS, the maximum deviation only amounts to $+40^{\circ}$ after the curve has proceeded to 30 per cent. MnS. It is as though the curve had, in consequence of the rapid rise, somewhat overstepped the values of the binary system. Above 30 per cent. the maximum variation is about $\pm 10^{\circ}$ up to 100 per cent. MnS, a deviation which at temperatures of 1400°C . to 1600°C . may well be assumed as lying within the errors of observation.

We may consequently conclude from the surprising agreement between the freezing-points of both bodies (which also behave alike, both physically and chemically and in every respect), that on the reaction of manganese sulphide on the eutectic Fe - FeS the combination $\text{Fe}_3\text{Mn}_2\text{S}_5$ also separates, and finally forms mixed crystals with a further MnS-excess.

The question of the reaction of the manganese sulphide on the eutectic mixture Fe - FeS can accordingly be answered in the following manner: By the addition of small quantities of MnS a ternary eutectic is first formed between iron and the two sulphides, in which, however, the manganese sulphide does not combine as such, but composes the eutectic mixture in a combination with FeS (as $\text{Fe}_3\text{Mn}_2\text{S}_5$) with free FeS and the iron. If the MnS-content rises above the eutectic composition, *i.e.* above about 4 per cent., the combination $\text{Fe}_3\text{Mn}_2\text{S}_5$ is primarily separated until finally, with higher MnS-contents,

a solid solution is formed between this compound and the MnS-excess.

It may be here objected that it would have been better to study the influence of an increasing MnS-content on the iron-ferrous sulphide eutectic on melts having exactly the eutectic composition 85 per cent. FeS and 15 per cent. Fe, melts which from the outset possessed no iron-excess. This is theoretically correct, but was found to be infeasible in practice, since it is not possible to make larger quantities of initial material of the exact eutectic composition and to avoid at the same time the slightest excess of iron. There was also the great danger of getting some hypo-eutectic melts showing a small excess of ferrous sulphide, and producing a reaction of the added MnS on this excess FeS, which at the very least would have given rise to uncertainty in the experimental data.

These considerations led to the decision of selecting as initial alloy a composition containing an always small excess of iron, so as to arrive as near as possible at the conditions forming the object of the investigation, namely, the study of the influence of manganese sulphide on the eutectic iron-iron sulphide enclosures deposited in the large excess of iron. The series of experiments carried out permitted (owing to the small excess of iron sulphide) a good survey of the thermal effects of the sulphides, which might have been impossible in the case of the larger iron-excess in consequence of the correspondingly smaller share of the sulphides in the composition. At the same time, there was but small possibility of the manganese sulphide being influenced by the free iron, in view of the slight excess of the latter.

SULPHIDES OF DIFFERENT MANGANISING STAGE IN THE LARGE IRON-EXCESS.

In order to study the effect of an addition of MnS on the small eutectic iron-sulphide enclosures deposited in iron and steel, and for the purpose of following the transition of the low MnS sulphide enclosures into the low FeS manganese sulphide enclosures, melts were made, each of 30 grammes electrolytic iron, to which were added each time small quan-

tities of one of the pure sulphide melts employed earlier in the study of the system $\text{FeS}-\text{MnS}$, and thus a series of melts having a content of 5 per cent. sulphide were obtained, in which both the proportion of iron and manganese sulphide in the composition of the aggregates, as well as their photomicrograph, were known.

These aggregates had, moreover, the advantage of complete homogeneity over the corresponding intimate mixtures of both sulphides, and the further advantage that the condition of equilibrium corresponding to the actual composition was attained. It was shown from comparative experiments that on adding mixtures of sulphides to electrolytic iron, ferrous sulphide and manganese sulphide occurred partially separated in the melts, the sulphides being hindered from mutually reacting by the intermediate iron. The method of working adopted corresponds to the desulphurisation processes actually taking place in practice—probably even to a greater extent inasmuch as it must be assumed here that on the one hand FeS is present, and, on the other hand, metallic manganese uniformly distributed over the iron bath. The metallic manganese can, however, only come into immediate contact with a sulphide particle for the primary formation of manganese sulphide, which latter can then immediately further react with the sulphide particle without being separated by inter-deposited iron. The thermal effects were not followed, since these were no longer perceptible so far as they related to the processes inside the sulphide layers. The sections were again tempered to yellow after a preliminary etching with picric acid.

These sections on again being examined with the microscope showed that a slight MnS -content in the sulphide enclosures was not perceptible. The sulphide appears as a fine network between the ferrite grains, and in the tempered state a beautiful light blue on a light-yellow ground (Fig. 24, Plate V.). If the MnS -content in the aggregates rises still higher, there will be noticeable the interesting fact of the occurrence in the sulphide network (whose veins become thicker and wider as if they had been viscid at the same temperature) of crystal layers which are scarcely observable

on the polished section, but which, however, after etching-tempering, appear very plainly—especially with daylight illumination—as faded-white to light-yellow enclosures in the dark-blue sulphide network (Figs. 25, 27, &c., Plate VI.). It is characteristic that these light crystalline enclosures in the sulphide network always occur in the thickenings produced by the collision of a number of ferrite grains, and the fine sulphide veins radiate between the individual ferrite grains.

Now, according to the preceding investigation, the combination $\text{Fe}_3\text{Mn}_2\text{S}_5$ is present in the light crystalline enclosures, while the remaining sulphide network is to be taken as the previously described ternary eutectic in which are embedded the primarily separated crystals of the combination $\text{Fe}_3\text{Mn}_2\text{S}_5$.

The process of freezing is in accordance with the form of curve found for the freezing of the sulphides, and is in perfect agreement with the microscopical results in this series of melts. The process is as follows: On cooling, the electrolytic iron first crystallises out of the melt, compressing the sulphide-iron eutectic in the spaces between the individual ferrite crystals, where it freezes and forms a network. If, however, the MnS-content in the sulphide-iron mixture exceeds the eutectic composition, then after the electrolytic iron has frozen out of the residual liquor the compound $\text{Fe}_3\text{Mn}_2\text{S}_5$ will primarily freeze, filling up the nodal points to a greater or lesser extent, and forcing the thinly liquid eutectic into the fine interstices of the ferrite grains. With increasing MnS-content the separation of the primary crystals $\text{Fe}_3\text{Mn}_2\text{S}_5$ naturally increases also, the residual eutectic decreasing. Finally, after the electrolytic iron, we have a solid solution, consisting of $\text{Fe}_3\text{Mn}_2\text{S}_5$ and MnS separating out in the melts: the freezing-point, however, of this solid solution soon exceeds that of the electrolytic iron, which is about 1510°C ., so that the sulphide mixed crystals then freeze before the iron, and contract in the form of roundish spherical products (Fig. 26, Plate VI.).

This series of experiments accordingly provided full confirmation of the conditions which one would expect theoretically from the preceding investigations.

Attention may be drawn here to the great similarity of the

photomicrographs of this series of melts with some photomicrographs published by Le Chatelier and Ziegler¹ in their work on iron sulphide; their photomicrographs being obtained from melts for which, according to their data, a mixture of iron, manganese, and sulphur was melted down by the Goldschmidt process. They made these melts for the purpose of determining the possibility of the entire sulphur contents of the melts combining with the manganese. Le Chatelier makes the following remark in this connection: "On voit très nettement sur la figure 24 (Gr. = 650) reproduisant l'apparence d'un procédé Goldschmidt, des globules jaunes de sulfure de fer, au milieu desquels on reconnaît aisément des cristaux de sulfure de manganèse." Le Chatelier thus assumes that the nuclei in the sulphide enclosures, which appeared dark when observed by him (since it was a question of polished sections or of sections only weakly etched with picric acid), are crystals of manganese sulphide embedded in iron sulphide. He thus excludes the possibility of a mutual solubility or the formation of a chemical combination of both sulphides.

According to the results set forth in this study, it must be assumed, from the description given by Le Chatelier of the manner in which the melts were made, that it is in the present case, as in the above melting experiments, a question of primarily separated crystals of the combination $\text{Fe}_3\text{Mn}_2\text{S}_5$ in the excess sulphide eutectic, *i.e.* a question of enclosures still fairly rich in FeS, but which in their properties approximate to the pure manganese sulphide. Pure manganese sulphide, or even only solid solutions of the same with the compound $\text{Fe}_3\text{Mn}_2\text{S}_5$, is excluded, since these crystals actually occur in common with "iron sulphide," in which they are embedded.

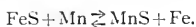
On the other hand, the view expressed in the literature is also inconclusive if, as it is assumed from the varying colour of different sulphide enclosures, it is a question of manganese sulphide in which more or less ferrous sulphide is dissolved; that is to say, that a continuous series of solid solutions or mixed crystals exist between ferrous sulphide and manganese sulphide. Thus, Law² states: "The

¹ *Loc. cit.*² *Loc. cit.*

sulphide occurring in steel varies very much in colour and composition. In some steels it is so pale in colour that it is difficult to photograph, whereas in others it is so dark that it may easily be mistaken for manganese silicate. The lighter colour is found in steels high in sulphur and low in manganese, and is probably due to the manganese sulphide dissolving a certain amount of iron sulphide."

The varying degree of colour of the sulphides observed on sections which were only polished may be attributed rather to varying preliminary treatment of the sections when grinding, &c., as was observed in sections containing pure iron sulphide enclosures.

It was also possible to determine at the same time, from the above described melting experiments on electrolytic iron with the addition of sulphides of different stages of manganisation, that on adding the sulphides to pure iron a conversion running from right to left, and dependent on the law of mass-action, took place in accordance with the equation



Thus a certain re-sulphurisation occurred and showed itself in the photomicrographs, so that the condition which would actually be expected from the composition of the melts of the system $\text{FeS} - \text{MnS}$ used as an aggregate, was never attained, but only took place with a higher MnS -content of the aggregate. Thus it was only possible to determine the occurrence of the primarily separated compounds $\text{Fe}_3\text{Mn}_2\text{S}_5$ when original melts containing about 15 per cent. manganese sulphide were used, while on adding the pure compound $\text{Fe}_3\text{Mn}_2\text{S}_5$ to electrolytic iron, a eutectic network was observed to re-form (Fig. 27, Plate VI.).

INFLUENCE OF THE CARBON CONTENT ON THE SULPHIDE ENCLOSURES.

In order to determine also whether a carbon content, such as occurs in malleable iron and steels, exerts an influence on the sulphide enclosures, the above-mentioned melting experiments on electrolytic iron with sulphide additions were extended to iron-carbon alloys also.

For this purpose a high percentage, pure iron-carbon alloy was first made by melting down electrolytic iron in a carbon tube. By adding definite quantities of this alloy (of 2·8 per cent. carbon content) to additional electrolytic iron, it was possible to obtain in the simplest manner alloys of any desired degree of carburisation.

The result of these experiments was the absence from the photomicrograph of any influence of the carbon content of the melt on the degree of manganisation of the sulphide enclosures. Only the form of manifestation of the enclosures was changed, in that when the carbon content was increased (*i.e.* with increase of pearlite), the eutectic sulphide network showed, when the composition was the same, a tendency to contract into spots, since the network appeared to be concomitant with the occurrence of the ferrite; and this fact is probably explained by the strong desire of the ferrite to crystallise, which simply deforms the still liquid sulphide enclosures, and presses them into the interstices of its crystalline structure. This behaviour of the "iron sulphide" has, moreover, been observed by others.¹

Of course the lower position of the freezing-point of the iron-carbon alloy has a certain amount of influence on the form of the sulphide layers; the higher the alloy is carburised, the lower the melting-point, and thus the earlier the freezing-point of the manganese sulphidic-sulphides passes beyond that of the iron-carbon alloy; so that accordingly, when regarded purely superficially, the separation of the sulphide enclosures into roundish spots takes place at a much slighter degree of manganisation of the sulphides.

Further reference will be made to the question—so important for desulphurisation—of the lowering of the freezing-point of the iron-carbon alloy, which is also brought about in practice by the use of other admixtures.

Figs. 28 and 29, Plate VI., contain two photomicrographs of iron-carbon alloys containing sulphide, and with a carbon content of 0·2 per cent. and 1·2 per cent. respectively, thus corresponding to a soft and to a very hard steel. Both show

¹ Cf. Liesching, *Über den Einfluss des Schwefels auf das System Fe-C.*, p. 14, Dissertation.

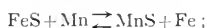
the light-coloured layers of the primary $\text{Fe}_3\text{Mn}_2\text{S}_5$ in the otherwise darkly-coloured sulphide enclosures. In both cases, the sulphide addition introduced was the compound $\text{Fe}_3\text{Mn}_2\text{S}_5$; thus here also re-sulphurisation has occurred through the withdrawal of manganese. It should be mentioned that these two sections (in which the pearlite appears almost black and the ferrite and cementite respectively light-coloured) were over-etched as regards these structural elements, since the principal data in view was to render the structure of the sulphide enclosures plainly perceptible. In this connection it was not possible to obviate the ferrite appearing considerably roughened, and, in parts, turned very dark in the photographs.

INFLUENCE ON THE SULPHIDE ENCLOSURES OF A MANGANESE CONTENT IN THE MELT.

Since it was found from the above melting experiments that on adding the sulphides to pure electrolytic iron the equation

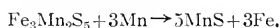


took a course from right to left (*i.e.* that re-sulphurisation took place to a certain extent), it appeared desirable to carry out experiments to determine what excess of manganese the bath must contain to prevent a re-formation of ferrous sulphide by the action of iron on the manganese sulphide. For this purpose a calculated quantity of manganese, in the form of ferromanganese, was first of all added to the molten electrolytic iron, the sulphide-addition being made only when the melt had been thoroughly mixed up. Melts containing 0.2 per cent. to 1.5 per cent. manganese were investigated in this manner, and it was found that only when the percentage of manganese was 0.8 was the excessive manganese sufficient to prevent a reaction from right to left according to the equation



in other words, on the addition of the compound $\text{Fe}_3\text{Mn}_2\text{S}_5$ to melts containing at least 0.8 per cent. manganese, a re-formation of eutectic no longer took place (Fig. 31). If the

manganese content of the melts rose higher, a reverse reaction of the manganese content on the sulphides took place; that is to say, the desulphurisation proceeded in the sense of the above equation from left to right. On the addition of sulphides with under 40 per cent. manganese sulphide, the eutectic disappeared more and more, with increased primary separation of the compound $\text{Fe}_3\text{Mn}_2\text{S}_5$, while on the addition of the pure compound $\text{Fe}_3\text{Mn}_2\text{S}_5$ a ferric nucleus often occurred in the sulphide enclosures of the resultant melts (Fig. 32). Obviously a reaction of the large manganese excess has taken place on a part of the combination $\text{Fe}_3\text{Mn}_2\text{S}_5$, as expressed by the equation



The manganese sulphide formed from this reaction forms solid solutions with the unconverted $\text{Fe}_3\text{Mn}_2\text{S}_5$, while the iron left free is forced towards the centre, since this reaction proceeds from the contact area of the sulphide globules with the manganese-excess of the bath, that is from the exterior to the interior.

The photomicrographs, Fig. 30 (Plate VI.) and Figs. 31 and 32, which were obtained from melts of electrolytic iron with increasing manganese content, show very characteristically the difference in appearance of the sulphide enclosures in the individual melts. These were obtained on the addition of the same sulphide alloy—the compound $\text{Fe}_3\text{Mn}_2\text{S}_5$. Fig. 30, Plate VI., with 0.4 per cent. manganese, scarcely differs from that of the same sulphide-addition in pure electrolytic iron (Figs. 27 and 30, Plate VI.).

On the other hand, Fig. 31 (0.8 per cent. manganese) no longer shows any eutectic, but only light-coloured roundish enclosures. Carbon is of course introduced into the melts by the ferro-manganese addition, and consequently the sections were in this case also over-etched in relation to the structural elements of the iron, since special importance was attached to securing good development of the structure of the sulphide enclosures.

It appears from these melts that a certain excess of manganese is necessary in the melts before a permanent desulphurising action of the manganese is possible. Of course

PLATE II

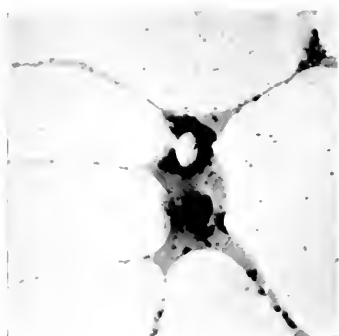


FIG. 1.—Magnified 350 diameters.
(Pp. 41, 55.)

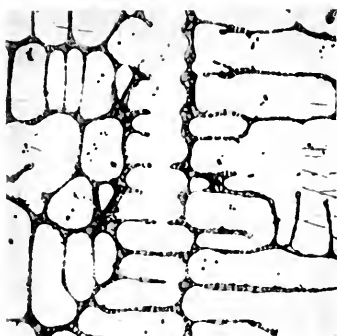


FIG. 2.—Magnified 85 diameters.
(Pp. 41, 55.)

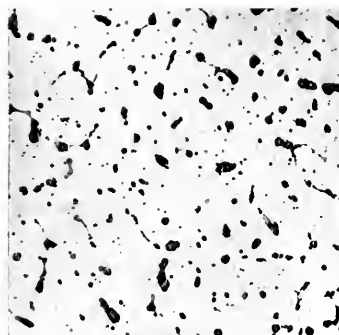


FIG. 3.—Magnified 85 diameters.
(P. 41.)

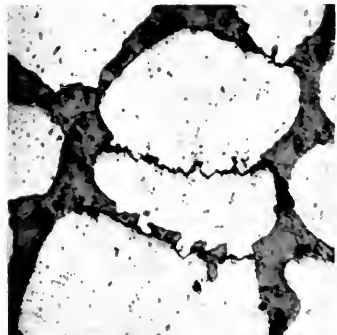


FIG. 4.—Magnified 350 diameters.
(P. 44.)

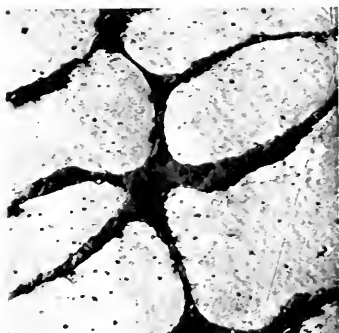


FIG. 5.—Magnified 350 diameters,
(P. 46.)

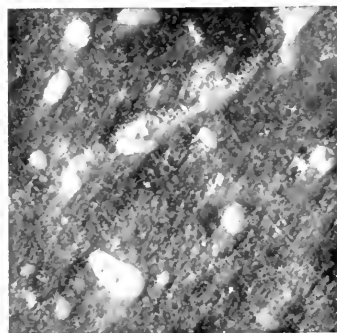


FIG. 6.—Magnified 350 diameters.
(P. 46.)



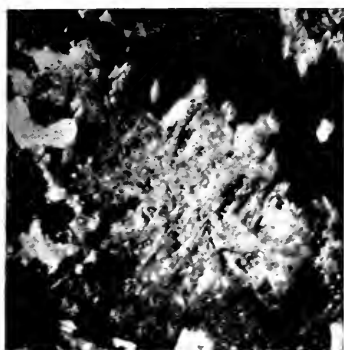


FIG. 7.—Magnified 350 diameters.
(P. 53.)

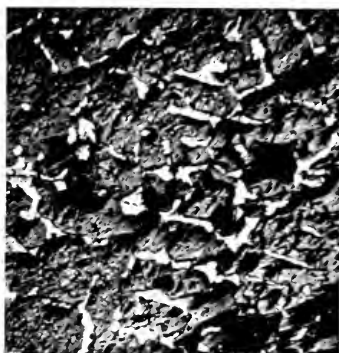


FIG. 8.—Magnified 170 diameters.
(P. 53.)

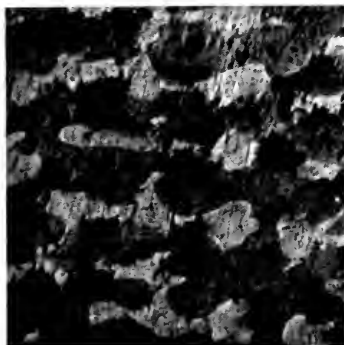


FIG. 9.—Magnified 170 diameters.
(P. 53.)

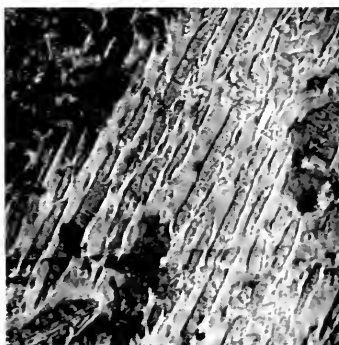


FIG. 10.—Magnified 170 diameters.
(P. 54.)

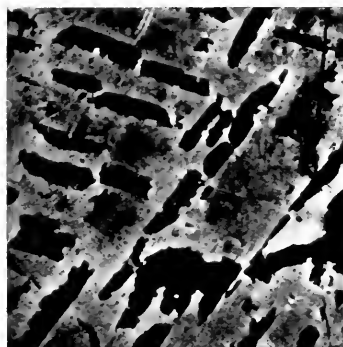


FIG. 11.—Magnified 350 diameters.
(P. 54.)

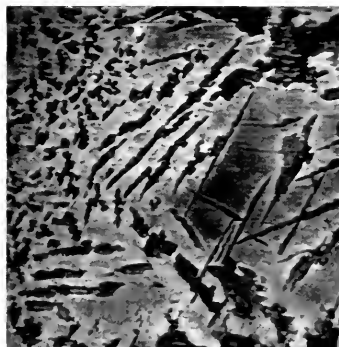


FIG. 12.—Magnified 170 diameters.
(P. 54.)

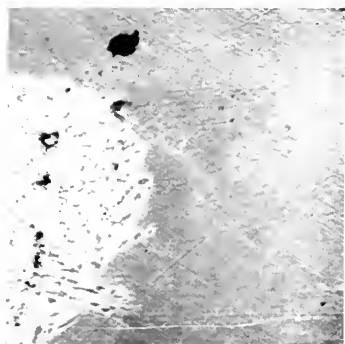


FIG. 13.—Magnified 170 diameters.
(P. 54.)



FIG. 14.—Magnified 170 diameters.
(P. 54.)

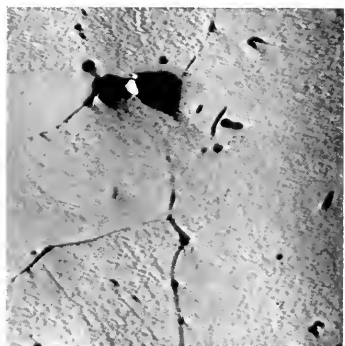


FIG. 15.—Magnified 170 diameters.
(Pp. 51, 54.)

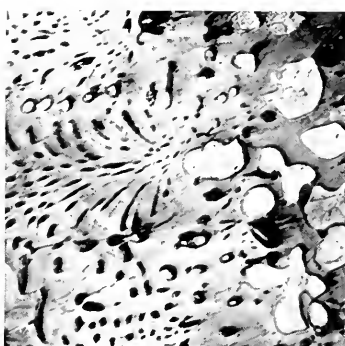


FIG. 16.—Magnified 170 diameters.
(P. 61.)

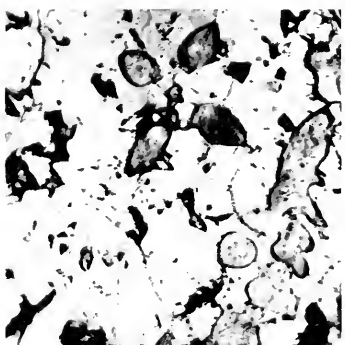


FIG. 17.—Magnified 170 diameters.
(P. 61.)

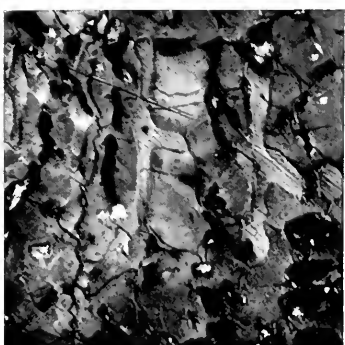


FIG. 18.—Magnified 170 diameters.
(P. 62.)

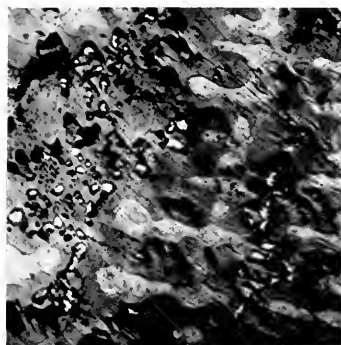


FIG. 19.—Magnified 125 diameters.
(P. 62.)



FIG. 20.—Magnified 250 diameters.
(P. 62.)

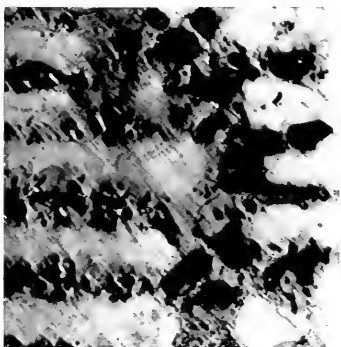


FIG. 21.—Magnified 170 diameters.
(Pp. 62, 63.)

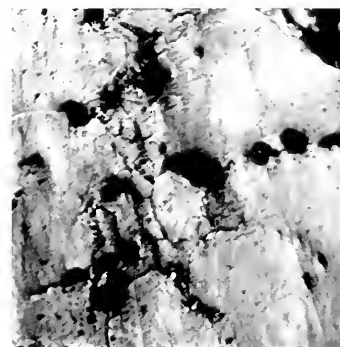


FIG. 22.—Magnified 170 diameters.
(P. 63.)



FIG. 23.—Magnified 170 diameters,
(P. 66.)

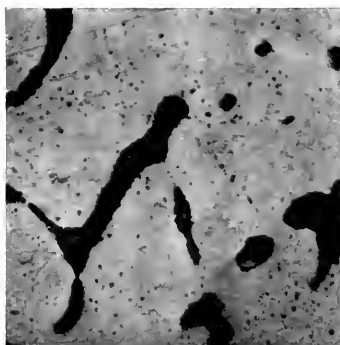


FIG. 24.—Magnified 350 diameters,
(P. 66.)

PLATE VI

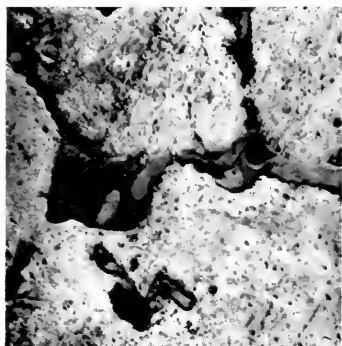


FIG. 25.—Magnified 350 diameters.
(P. 67.)

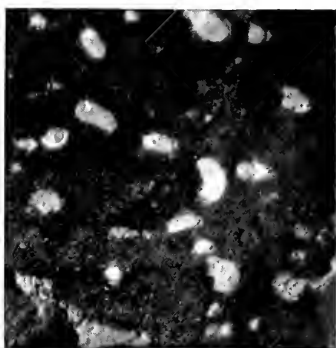


FIG. 26.—Magnified 350 diameters.
(P. 67.)

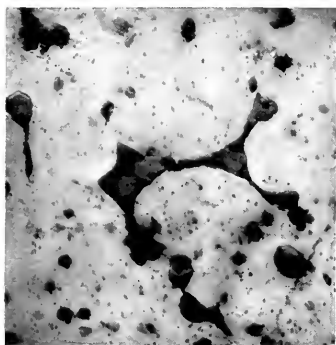


FIG. 27.—Magnified 350 diameters.
(Pp. 67, 69.)

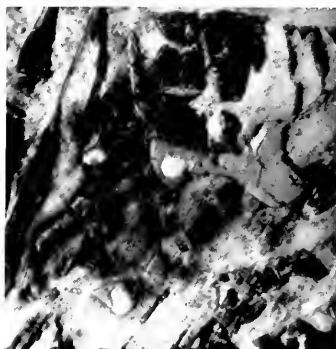


FIG. 28.—Magnified 350 diameters.
(P. 70.)

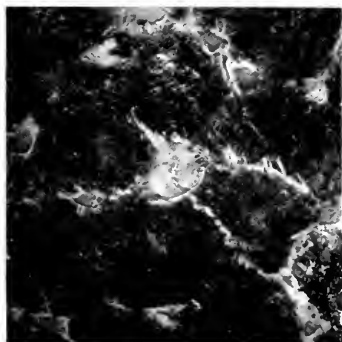


FIG. 29.—Magnified 350 diameters.
(P. 70.)



FIG. 30.—Magnified 350 diameters.
(P. 72.)

the 0·8 per cent. manganese found from these experiments to be requisite may not fit in with facts such as occur in practice; fortunately, considerably smaller manganese excesses suffice in practice. The reason for this is probably chiefly the disproportionality in the differences of the charges. In these experiments charges of 30 grammes were used, and they naturally solidified very rapidly, and left but little time for the reaction.

Ledebur states in his work on "The Metallurgy of Iron," vol. iii. p. 234, in connection with the manufacture of mild steel: "The richer the iron is in sulphur, however, the more necessary is it that an excess of manganese should remain in

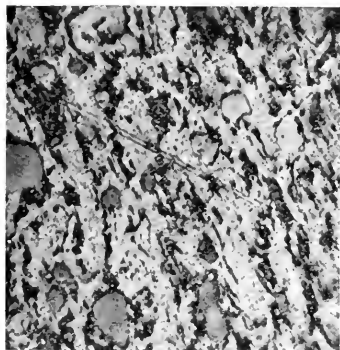


FIG. 31.—Magnified 350 diameters.

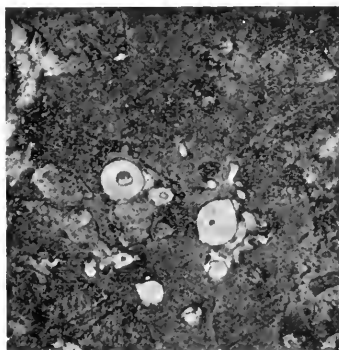


FIG. 32.—Magnified 350 diameters.

the iron. It is therefore customary to fix the quantity of the manganese-addition so that the finished iron still contains at least 0·25 per cent. manganese, and occasionally the residual manganese content exceeds 1 per cent."

Unfortunately, the author had not at his disposal the arrangements for studying the influence of the manganese excess on the sulphides with larger charges also. It would certainly be a great source of satisfaction if, when opportunity offered, exhaustive experiments could be carried out on charges of varying magnitude.

In glancing now over the data found from the investigations on the constitution of sulphide enclosures, the most important fact will be the circumstance that in the reaction of the man-

ganese sulphide on the iron sulphide, a compound is soon formed, with the result that the properties of the sulphide enclosures undergo, so to speak, a valuable improvement, for this compound $\text{Fe}_3\text{Mn}_2\text{S}_5$ (although still containing 60 per cent. ferrous sulphide) closely approximates in its physical properties to the pure manganese sulphide. While the melting-point of the eutectoid sulphide mixture lies at 980°C. , it was, in the case of this compound, determined as 1365°C. , and the sulphide alloy has become tenacious in comparison with the brittle, crumbly, ferrous sulphide.

Pure manganese sulphide, and even the solid solutions of the combination with MnS , would scarcely be attained practically in the desulphurisation, since they could only form by a reaction of manganese on the compound $\text{Fe}_3\text{Mn}_2\text{S}_5$ (with partial decomposition in accordance with the equation $\text{Fe}_3\text{Mn}_2\text{S}_5 + 3\text{Mn} = 5\text{MnS} + 3\text{Fe}$), producing manganese sulphide, which afterwards forms solid solutions with the undecomposed portion of the compound. However, as it follows from the experiments, a large manganese excess and a long period of reaction are necessary for carrying through this change to any great extent.

It is therefore assumed that the compound $\text{Fe}_3\text{Mn}_2\text{S}_5$, which does not differ greatly in appearance from pure manganese sulphide, has hitherto often been taken for pure manganese sulphide; and when Law¹ states, "As a rule, manganese sulphide is not broken up, but rolled out into long threads," it may be a question in this connection not of pure manganese sulphide, but of this compound. Probably there is here also the key to the discordance when he resumes: "And it is difficult to reconcile this fact with the statement made by Le Chatelier that manganese sulphide has a higher melting-point than iron."

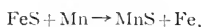
It would be a very useful work to test numerically, for their physical behaviour, the different melts between iron sulphide and manganese sulphide—probably by making fairly large melts, casting these in suitable moulds, and testing the pieces thus obtained for their hardness, tensile and compressive strength, &c. This, of course, would necessitate smelting

. ¹ *Loc. cit.*

arrangements which, giving temperatures of up to 1700°C ., would permit the simultaneous melting down of large quantities of sulphide without the admittance of air—an equipment which cannot be very easily provided. In such an investigation it would be possible to accurately determine numerically—as has already been found on grinding and treating the melts—that when the combination $\text{Fe}_3\text{Mn}_2\text{S}_5$ has been attained, a striking improvement takes place in the physical properties; the tensile and compressive strength curves in particular would rise considerably, altering but slightly with higher MnS-additions up to pure manganese sulphide. The author would be glad if the suggestion which he now makes could be carried out and further investigations instituted in this direction, as they appear to him to be of not inconsiderable importance.

THE IMPORTANCE OF MANGANESE IN DESULPHURISATION.

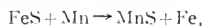
The view is pretty widely held, and, among others, by Ledebur (*cf.* p. 73), that manganese plays an important part in the desulphurisation of the iron bath. In the present investigation material may have been provided for a recognition of this theory; the desulphurisation of the iron bath increases and decreases with the action of the manganese in accordance with the conversion



which fact has been observed in numberless instances in practice.

The segregation of the sulphur, that is, the tendency to irregular distribution in the material, is, of course, very considerable in the case of pure iron sulphide, since the freezing metal presses, towards the centre, the thinly liquid $\text{Fe} - \text{FeS}$ eutectic. Thus, for instance, there is found normally in large ingots poor in manganese the greatest sulphur-enrichment, which occurs at the centre and at the end of the ingot.

The favourable influence of the properties and a separation in the liquid iron bath only occur when, in accordance with the equation

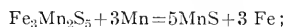


the conversion has been produced by a manganese-content of the bath. This manganese sulphide is not, however, as

may have been shown by this research, the final result of the desulphurisation processes, but at once forms the combination $\text{Fe}_3\text{Mn}_2\text{S}_5$ with a part of the iron sulphide still present, absorbing in this manner a very important part of the free iron sulphide; and therefore equal importance attaches to the formation of this compound as to the change from iron sulphide into manganese sulphide producing the desulphurisation. This compound is very important, as it so considerably improves the qualities of the sulphur combined in it. It is, in particular, much more difficult to melt than the $\text{Fe}-\text{FeS}$ eutectic, and thus freezes at much higher temperatures of the iron bath—in many instances earlier than the iron. The frozen globules have a great tendency, owing to their low specific gravity, to rise up in the melt and hence emerge from the bath. In this tendency to separate out, the manganiferous sulphide is finally overtaken by the freezing metal and partially enclosed, being for the greater part, however, driven forward with the fluid mother-liquor towards the centre.

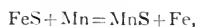
But the enclosures in the iron held fast by the freezing of the iron are not nearly so dangerous to the use of the material when occurring in the form of the compound $\text{Fe}_3\text{Mn}_2\text{S}_5$, since, as has already been found, this compound possesses a certain degree of tenacity, so that on rolling and drawing down, the enclosures do not break up easily, but are capable of undergoing deformation (*cf.* Law, p. 74).

It is, as has already been mentioned, very improbable that this compound $\text{Fe}_3\text{Mn}_2\text{S}_5$ will go to form solid solutions with manganese sulphide owing to being further influenced by the manganese content of the bath, since for this purpose a partial re-decomposition would be necessary in accordance with the equation



the formation of solid solutions between $\text{Fe}_3\text{Mn}_2\text{S}_5$ and MnS also requires a longer action of a considerable excess of manganese in the bath. Practically little importance attaches to this higher manganisation of the sulphide enclosures, since the properties of this solid solution are not different from those of the compound $\text{Fe}_3\text{Mn}_2\text{S}_5$, with the exception that the freezing-point is still higher.

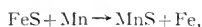
From the fact that (according to the formula $\text{Fe}_3\text{Mn}_2\text{S}_5$) much less manganese is used for obtaining a favourable degree of desulphurisation than for producing a change simply in accordance with the equation



with pure manganese sulphide as a final product, it follows (since every reaction requires a certain time) that actually the attainment of a favourable degree of desulphurisation is more quickly reached than a change would be according to the equation given above.

The reaction, however, always requires so much time that it cannot be carried out right to the end—in the case of a certain proportion of metallurgical processes—before the iron bath freezes and interrupts the further process of the conversion and separation of the sulphur. An acceleration of the change, that is a desulphurisation in a short period, could, of course, be attained by a large excess of manganese in the bath. Somewhat narrow limits are set in practice to this method of accelerating the desulphurisation, which is to a certain extent customary in the Bessemer basic and open-hearth processes when recarburising by the simultaneous introduction of manganese alloys: the reason for this limitation being that the manganese-excess forms with the iron a continuous series of mixed crystals, thus adversely influencing the properties of the material when certain values are exceeded.

A second possible method of producing favourable desulphurisation is to have the manganese content low and to leave the bath as long a time as possible to complete the reaction



and to separate the $\text{Fe}_3\text{Mn}_2\text{S}_5$ resulting as a final product owing to the difference in specific gravity. This method has been carried out for many years in crucible smeltings; but melting in a crucible has simply to be considered as a re-melting in which sufficient time is given to the impurities to emerge from the bath, while the latter is kept consistently thinly liquid by the introduction of heat from the outside.

In the case of pig iron the same purpose is fulfilled by the mixer.

More recently this method has also been introduced in the production of electro-steel. The production of steel in the electric furnace is indeed simply to be regarded as a refining of the ordinary steel, the most valuable fuel—the electric current—being used, and entirely excluding renewed deterioration of the bath by solid and gaseous substances such as must be produced by coal, coke, and generator gas. Specially the last period of the melting of steel in the electric furnace (that is after the re-carburising material has been added) permits of the sulphur being driven out to the very last trace. This is designated the perfect refining period, and its purpose is principally to allow time for the manganese content of the bath to react on the iron sulphide, and to give to the iron-manganese sulphide combination produced by this change an opportunity of leaving the melt which is obtained by heating in a suitable thinly liquid state.

Röchling, for instance, stated in a lecture, held on the occasion of an excursion meeting of the German Society of Chemists (Saxon-Thuringian Section), at Freiberg in July 1911, that it was possible with 0.25 per cent. manganese to separate the sulphur to the last traces by leaving the molten steel quiescent for some time. The complete absence of segregations and pipes was shown in comparative photographs of ingots and rolled materials of basic steel and electric iron by the Röchling-Rodenhauser method. In this connection the following figures are interesting :—

	Basic Steel.	Electric Steel.
Strength, kilogrammes . . .	38-44	61-65
Extension, per cent.	22-24	17-18
Elastic limit, kilogrammes . .	28	41.6-45.4

It may not be uninteresting, in view of the processes derived from the foregoing research for the desulphurisation, to give an observation made at a German blast-furnace and brought accidentally to the author's knowledge. The fact—at first glance somewhat surprising—was noticed that hot iron in the mixture was not so well desulphurised as thickly liquid iron. If it be assumed, as was done previously, that

desulphurisation ensues by separation of the sulphur in the form of manganese sulphide, then (since the melting point of manganese sulphide has been determined at 1600°C ., and is thus in any case present in the iron bath of the mixer as a solid body), in the case of hot or thickly liquid iron, one would rather incline to the assumption that a change would be more energetic with greater heat and that the separation would rather be more considerable in view of the contents of the mixer being in a more thinly liquid state.

It is otherwise, however, in the case of the formation of the intermediate stage $\text{Fe}_3\text{Mn}_2\text{S}_5$. Its freezing point is lower, having been found to be 1360°C . It is therefore quite conceivable that in the case of hot iron the iron-manganese sulphide formed still floats about in the melt in the form of small drops, which may easily sputter by the motion in the bath in consequence of the ease of displacement of the individual particles: while, in the case of thickly liquid iron, the temperature may be so favourable that the iron-manganese sulphide $\text{Fe}_3\text{Mn}_2\text{S}_5$ formed by the reaction of the manganese freezes, and, as a frozen body, has a much greater tendency to separate according to specific gravity, the iron bath still remaining liquid at the existing temperature. Specially favourable conditions for desulphurisation consequently exists at the temperature of the but slightly overheated thickly liquid iron.

Mention may be made here again of the fact observed by Wüst, namely, that the sulphide crystals froze before the main mass of metal in the case of iron rich in carbon, and afterwards in the case of a material poor in carbon (*cf.* p. 51). Pure manganese sulphide, having a melting point of 1620°C ., would, even in chemically pure iron free from carbon, freeze before the remainder of the iron bath, since the latter has a melting point of 1510°C .

THE INTERCRYSTALLINE FRACTURE OF IRON AND STEEL.¹

By J. C. W. HUMFREY, B.A., M.Sc., M.Eng.,
OF THE NATIONAL PHYSICAL LABORATORY.

THE mechanism of the deformation and fracture of metals as revealed by the microscope has been studied particularly by Ewing, Rosenhain, and the present author; and it has been shown that when a normal specimen of metal is mechanically strained beyond its elastic limit, the material accommodates itself to the strain by a series of slips taking place along the gliding planes of the irregularly outlined—but truly crystalline—grains of which the mass is built up. In materials which possess more than one component, such as a normal 0·3 per cent. carbon steel, these slips are chiefly confined, in the earlier stages of deformation at least, to the softer component (in this case the ferrite). But whether the material is composed of one or of more than one components, it is usually a well-marked fact that the joints between either the individual crystals or the different components are considerably stronger than the gliding or cleavage planes within them; and if the straining is continued until the specimen is broken, it is found that the line of fracture runs almost entirely through the crystals and not along the boundaries between them.

This fact is very completely illustrated in a series of experiments described by Rosenhain.² By electrically depositing copper upon the fractured end of broken test-pieces he was able to obtain a section of the fracture which could be polished for microscopic examination without any damaging or rounding of the fractured edge. Specimens of iron and steel broken by tension, shock, and bending were examined by this method, and in all cases the fracture was found to pass

¹ Received February 29, 1912.

² "Deformation and Fracture in Iron and Steel," *Journal of the Iron and Steel Institute*, 1906, No. II.

through the crystals and not round them. The author, in conjunction with Ewing,¹ has shown that repeated alternations of stress cause a similar result, the slipping in this mode of fracture occurring backwards and forwards along the gliding planes of the crystals until a lack of cohesion results—due to the wearing action of the two surfaces upon one another—and some of the planes of slip become actual cracks.

In certain cases in which a small quantity of one metal is alloyed with another which is originally quite ductile, the eutectic which separates after the crystals of the metal in excess have solidified forms a brittle or weak envelope around them. This eutectic may be almost invisible under the microscope, but causes the metal, when strained, apparently to break round the crystalline boundaries. Such cases have been studied by Arnold, Osmond, and Stead, and may be classed as the usual form of cleavage fracture, since the material breaks through a constituent, viz. the weak eutectic envelope, and not in the boundaries between this constituent and the crystals of the pure metal. Stead,² however, mentions cases in which no weak envelope is present, but in which fracture occurs along the crystalline boundaries—such a fracture being found in certain annealed steels containing phosphorus.

The author, in the course of his work at the National Physical Laboratory, had occasion to examine two exceedingly interesting cases of materials which possessed a marked intercrystalline weakness, one a boiler plate³ and the other a sample of pure electrolytic iron, and was led to investigate how the crystalline structure of a metal could be so modified from its normal condition as to produce the phenomenon of intercrystalline weakness.

Intercrystalline weakness has since been found in a sample of transformer sheet, and the author has been successful, by suitable heat treatment, both in producing this condition in Swedish iron and also in restoring the brittle material to its original condition in which the fracture invariably passes through the cleavage planes of the crystals.

¹ *Philosophical Transactions of the Royal Society, A.*, 1902, pp. 241-250.

² *Journal of the Iron and Steel Institute*, 1898, No. II. p. 140.

³ The report of the National Physical Laboratory upon the defects of this boiler plate have been published as a Departmental Paper (No. 231) by the Board of Trade.

INTERCRYSTALLINE BRITTLENESS IN ELECTROLYTIC IRON.

The electrolytic iron was originally made for the purpose of obtaining as pure a material as possible for experiments on the structure of iron at high temperatures. It was deposited from an electrolyte consisting of a strong aqueous solution of ferrous and calcium chlorides, maintained at a temperature of 110° C., with a current density of about 20 amperes per square decimetre.¹ An iron cathode with flat faces (about 2 inches by 1 inch) was usually employed, and it was found that a more uniform deposit could be obtained by carefully polishing the faces. Under the above conditions a deposit of about $\frac{1}{8}$ inch thick was obtained in about forty-eight hours.

The iron was deposited in a fairly soft state, and with care the slabs could be separated in one piece from the cathode. It was however decidedly "rotten" and the slabs were easily broken. The outer surface was somewhat rough and tree-like growths always formed on sharp corners or edges of the cathode. The surface in contact with the polished surface of the cathode possessed a smoothness and polish equal to that on which it was deposited.

A polished and etched section of a slab examined under the microscope showed a very irregular structure, the crystals in the edge nearest the cathode being exceedingly minute but gradually increasing in size as they grew outwards from it. The surface of the crystals, after etching, showed peculiar wavy markings and also numerous small cavities, probably filled with electrolyte. These features are shown in Figs. 1 and 2, Plate VII. The iron as deposited showed a marked tendency to rust on exposure to the air. For the purpose of the experiments for which it was originally intended the iron was required in the form of thin strips, and since the material as deposited was too weak to be rolled it was necessary first to anneal it. To prevent any contamination of the iron, it was decided to do this *in vacuo*, and electrically heated glazed porcelain tube furnaces were constructed for the purpose. The construction of these furnaces is described in the appendix.

The deposited slabs were annealed at a temperature of

¹ This process is the subject of a patent, described in *Metallurgie*, Nov. 1909, p. 699.

about 1000°C . for two or three hours and then slowly cooled, the vacuum being sufficiently high to prevent any oxidation, so that they remained perfectly bright. When etched after annealing they showed a massive structure of irregularly shaped ferrite grains easily visible to the naked eye, which in most cases passed completely through the slab from one side to the other. The surfaces of the crystals showed none of the wavy markings found on deposited material. The iron was now malleable and could be rolled into thin strips in the cold; if, however, any sharp bend was given to the slabs they at once broke with an extremely brittle fracture, and this fracture was found to follow the boundaries of the ferrite crystals.

In a paper by Dr. Rosenhain and the present author¹ it has been shown that when polished samples of iron are heated *in vacuo* and afterwards examined under the microscope, the surface is covered with a network of lines which apparently represent certain of the crystal systems which have existed during different temperature ranges corresponding to the various allotropic modifications of the iron. Kroll² has also studied the same effects by heating in non-oxidising gaseous atmospheres. This phenomenon has given valuable assistance during the present research, and in most cases some of the samples have been carefully polished before being placed in the furnace and the surface examined microscopically after annealing.

After heating polished samples of electrolytic iron to 1000°C ., two distinct systems of crystalline boundaries were visible:—

(1) A deeply marked network of polyhedra whose boundaries were represented by distinct V-shaped grooves in the surface. From the frequent parallel bands which terminate in these boundaries, and which are evidently signs of twinning, they have been identified as probably representing the outlines of the γ -iron existing above 890°C .

(2) A second and usually much larger network whose boundaries crossing those of (1) at random were revealed by

¹ *Proceedings of the Royal Society, A.*, vol. lxxiii., 1909, pp. 200–209.

² *Journal of the Iron and Steel Institute*, 1910, No. I. p. 304.

fine dark lines. These have been found both by etching and the examination of slip bands after straining, to correspond to the final system of α crystals which remain after cooling, and it was along these boundaries that the fracture took place. The intercrystalline fracture was particularly well marked in thin strips of electrolytic iron which had been reannealed *in vacuo* after rolling down in the cold from the annealed slabs. The crystals in these strips were found to grow to linear dimensions up to $\frac{1}{2}$ inch in length and breadth, and to pass right through the strip. Such strips could easily be broken up into their individual crystals by bending between the fingers. Fig. 3, Plate VII., shows a piece of this material, about twice natural size, after bending, and it will be seen that the crystals have started to break away from one another along the boundaries between them.

The experiment was tried of reannealing *in vacuo* such a single crystal, which had been necessarily slightly strained in separating it from its neighbours. After annealing it was found to have split up into numerous smaller crystals of different orientation. The new boundaries found within the originally uniformly oriented crystal possessed an exactly similar weakness to that which enabled this parent crystal to be separated from its neighbours. This fact seemed to dispose of the theory that the boundary weakness could be caused by any impurity which originally existed in the intercrystalline boundaries of the material as deposited and which had re-formed there after annealing, since such an impurity would be lacking after the original crystal had been broken away. Apart from this, microscopic examination of a polished unetched surface showed no sign of the boundaries, such as would be expected if foreign matter were present in any appreciable quantity; and even after etching the boundaries were only revealed as very fine lines, resembling those found in a normal structure of pure ferrite.

PURE REDUCED IRON.

With the idea of obtaining another exceedingly pure sample of iron which could be compared with that prepared electro-

lytically, the author was successful in fusing a small quantity of "ferrum reductum," prepared by reducing iron from a pure salt by means of hydrogen. After reduction from the salt the iron is in the form of a grey powder, and any attempt to fuse it in air at once causes it to burn. The author, therefore, carried out the fusion in a high vacuum. This was done in an electrically heated furnace with special windings, the construction of which is described in the appendix. A great deal of difficulty was experienced owing to the breaking and fusing of the platinum-rhodium wire used for the inner winding when sufficient current was passed through it to obtain a temperature above the melting point of the iron, but after many unsuccessful attempts a small ingot about $\frac{3}{8}$ inch diameter and $\frac{1}{4}$ inch long was obtained. One half of this ingot was hammered flat and then rolled out in the cold until a thin strip of iron was obtained. This was annealed *in vacuo* at about 1000° C., and then polished and etched. Except for some patches of grey matter somewhat resembling slag on wrought iron, the structure consisted of large ferrite grains. The specimen when strained in tension at once broke along the boundaries of the grains with very little deformation of the crystals themselves. The boundaries only appeared as very fine lines on etching, and the grey substance was found within the crystals themselves and not between them, and therefore could not tend to any weakness along the boundaries.

The fact that intercrystalline weakness was produced in two different varieties of pure iron prepared by different methods, by the process of annealing samples *in vacuo*, led the author to investigate whether a similar treatment would have the same effect upon commercial iron, and, if so, in what way the alteration in its normal structure was brought about.

TRANSFORMER SHEET.

The first commercial material selected for experiments on annealing *in vacuo* was a mild steel transformer sheet, which gave the following composition on analysis:—

	Per Cent.
Carbon	0.024
Silicon	0.098
Sulphur	0.026
Phosphorus	0.047
Manganese	0.495

Numerous strips of this material were annealed *in vacuo* under similar conditions to the treatment given to electrolytic iron, and in some cases a similar marked intercrystalline brittleness was obtained. In some of these experiments the samples were allowed to rest directly upon the bottom of the porcelain tube, while in others the samples were supported upon slabs of "Mabor" brick.¹

In the experiments performed under the latter conditions, *i.e.* with the specimen upon a Mabor slab, it was invariably found that the brittleness was very much more marked than in those performed under the former. The surface of the brittle specimens (which previous to the annealing upon Mabor had been polished for microscopic examination) were afterwards found to exhibit two distinct features, apart from the ordinary network of boundaries which are produced by a simple annealing *in vacuo*.

These features were:—

(a) A decided etching of the γ crystals, many of them showing distinctive series of geometrical etching figures.

(b) Numerous patches of a grey substance, which assumed in places a decided crystalline form.

A photomicrograph of the surface of a piece of transformer iron, after annealing for about three hours at 1000° C. upon a Mabor slab *in vacuo*, is shown in Fig. 4, Plate VIII. (magnified 1000 diameters). The dark boundaries are those of the γ crystals, to which the etching figures correspond, and an α boundary, appearing as a white line under the illuminator, is seen running across the top of the crystal.

The grey crystals of foreign matter, appearing almost black in the figure, were scattered irregularly both in the boundaries and upon the ferrite crystals, and were most numerous near the edges of the specimen. Subsequent experiments have shown

¹ This was done with the idea of keeping the samples out of contact with the glaze of the porcelain tube, and it was thought that the Mabor would have no action upon iron.

that the grey matter is probably an oxide of iron; on reannealing a sample in hydrogen it is reduced again to metallic iron, but a "scar" is left where the patch existed.

The fact that the presence of Mabor brick greatly increased the tendency to produce intercrystalline brittleness led to a series of experiments to determine to what action this was due. Soon after these had been commenced, however, the somewhat surprising fact was discovered that the material as obtained already possessed to a marked degree an intercrystalline *weakness*. The sheet did not at first sight appear brittle, and could be bent several times backwards and forwards without breaking; but if this process was carried on until fracture had commenced, and the specimen was then straightened and the surface ground flat, and then polished and etched, it was found on examination under the microscope that the fracture followed the intercrystalline boundaries; and that near it, where the straining had been severe, each crystal had broken away from its neighbours, leaving a distinct crack between them. A photomicrograph of the fracture of this material is shown in Fig. 5, Plate VIII.

The author has had some experience with this class of material, but has never before found a sample possessing such a fracture, and it is somewhat remarkable that it should have been unwittingly chosen for the present research.

The discovery of the peculiar nature of the transformer sheet rendered the results of the experiments performed upon it inconclusive, and a fresh material—a pure Swedish iron sheet—was therefore selected for further experiments; samples of this sheet were found in their normal state to possess a typical cleavage fracture.

EXPERIMENTS ON ANNEALING SWEDISH IRON *IN VACUO*.

Preliminary experiments at once confirmed the results of those obtained with the transformer sheet, viz. that marked intercrystalline brittleness could be obtained in strips of the material by annealing *in vacuo* upon Mabor slabs. Annealing for two hours at 1000° C. produced such extreme brittleness that if the strips were afterwards slightly bent, any attempt to

straighten them with a hammer at once resulted in a series of cracks forming along the crystalline boundaries. Previously polished samples showed the same etching effects upon the γ crystals, and in some cases, after prolonged annealing, the grey crystalline matter was present in such quantity as to practically mask the structure of the iron beneath.

In some of the experiments long strips of iron were used, and these were placed in the furnace so that part of their length lay outside the heated portion of the tube. By this method a range of temperature was obtained in the sample from 1000°C. (to which the centre portion of the furnace was heated) down to a temperature well below that of any change point in the iron. In the experiment now to be described, two of these strips were heated together over a range of temperature, a face of one of them having been previously polished. In this case the strips were supported upon a slab of Zirconia, which it was thought would have no action such as the Mabor; the furnace had, however, been previously used for experiments on Mabor, and it was evident from the appearance of the polished strip that traces of the etching reagent, evolved from the Mabor, still remained in the tube.¹

Three regions, showing distinctive sets of crystalline boundaries, were visible upon the surface of the polished specimen, corresponding to definite temperature ranges. These ranges have been shown by subsequent experiments, conducted at different temperatures, to correspond to intervals between the critical points of the iron.

The hot end, which had been at about 1000°C. , showed the usual double system of boundaries, such as are found in electrolytic and transformer sheet. This is shown in Fig. 6, Plate IX., magnified 300 diameters. The straight bands running across the γ crystal are evidence of twining, and the α boundaries are the fine black lines just visible at this magnification. This region corresponds to the γ state above Ar_3 . Further on towards the colder end of the specimen the γ boundaries disappeared and the α ones became more strongly

¹ Subsequent experiments have shown the effects produced to be due to CO_2 evolved from the Mabor on heating. It is known that this gas is exceedingly difficult to remove by pumping, and it is probable that traces of it remained in the tube.

defined. This is shown in Fig. 7, Plate IX., magnified 300 diameters. It will be seen that some of the crystals show an inner network of fine lines. This region corresponds to the β condition between Ar_2 and Ar_3 . Still further along the specimen these boundaries became still more strongly marked, and a deep etching became visible over the surface of the crystals. This part is seen in Fig. 8, Plate X., magnified 300 diameters, and also Fig. 9, Plate X., magnified 800 diameters. The latter photograph shows clearly the beautiful system of etching figures developed by the etching, and the deep groove formed along the boundaries. This region corresponds to the α condition between Ar_1 and Ar_2 . The etching effect ceased abruptly at about the centre of the specimen, and for about 1 inch beyond this the surface was covered with a dark tarnish, which gradually grew less marked, and the specimen at the cool end remained bright as before annealing.

An unpolished strip of similar size, which lay beneath the one just described during the annealing, was carefully marked so that the various regions, corresponding to those found upon the polished one, could be identified, and this strip was then broken in each region by bending backwards and forwards. In each of the three regions corresponding to those in the polished specimen in which crystalline boundaries had developed, the specimen was exceedingly brittle (in the γ region it broke after straightening out the first bend), but in the tarnished and unaltered areas several severe bends backwards and forwards were required to fracture it. After breaking, the pieces were all soldered in order on to a brass strip, the surface ground flat, and then polished and etched, so that each fracture could be examined under the microscope. Photomicrographs, Figs. 10, 11 (Plate XI.), 12, and 13 (Plate XII.), magnified 150 diameters, show the fractures in the three brittle regions (starting from the hot end), and the tarnished region respectively. It is evident that all the brittle fractures (Figs. 10, 11, 12) are distinctly intercrystalline, while the other (Fig. 13) is cleavage¹ and shows the

¹ In using the term "cleavage," the author does not mean it to imply a *sudden* break of the crystals such as can be produced in certain minerals, but rather the minutely stepped fracture which occurs after severe plastic deformation by slip. See Rosenhain's paper on "The Deformation and Fracture of Iron and Steel" (*loc. cit.*)

lines where slips, occurring during the alternations of stress in bending backwards and forwards, have reappeared on etching. The latter fracture is similar to that found in samples of untreated material.

This experiment shows that the brittleness is produced at all temperatures above the carbon change point, but that the change was most complete above Ar_3 and became less marked in the β and α regions. The latter fact is clearly shown in the photographs of the fractures by the greater deformation the crystals in the neighbourhood of the fracture have undergone, as the maximum temperature of annealing has been lower. The etching action in the α region—absent at higher temperatures—is particularly interesting, and it would appear that the action is limited to a definite temperature range, *i.e.* between Ar_1 and Ar_2 .

Besides the method described above of examining the nature of a fracture by repolishing the surface of the specimen and tracing the path of the fracture through or around the crystals, it has been found that a direct view of the fractured surface itself under low power objectives gave complete information as to its character. For visual observation of the fractures in this manner the author used a Greenough stereoscopic microscope by Zeiss. In testing the samples the strip was firmly held in a small vice or in parallel nosed pliers, and the free end bent backwards and forwards until the fracture occurred. The brittle samples usually broke when straightening after the first bend, and such samples could always be distinguished by giving out a curious crackling sound when bent, resembling the "cry" of tin.

The brittle fractures when viewed under the microscope showed an irregular surface composed of exceedingly bright facets, corresponding to the faces of the polyhedral ferrite crystals of which such a material is built up. A few sharp fine lines appearing upon some of the facets were apparently due to slips bands, caused by the slight deformation undergone by the crystals before the rupture along the boundaries. In the normal material, and in samples in which intercrystalline brittleness was not produced, the fracture showed none of the bright facets, but consisted rather of numerous little

irregular nodules and cavities, typical of the "hackly" fracture of ferrite along irregular cleavages after considerable deformation of the crystals. Although the visual observation of such fractures forms an efficient and simple method of determining whether they are cleavage or intercrystalline, their reproduction by photography presents some difficulty. Unless the fracture is illuminated by very diffused light, the light reflected into the camera from certain facets is so intense, compared with the general illumination of the surface, that an exposure sufficient to bring out the general details results in hopelessly fogging many parts of the plate. In the photographs shown, Figs. 14, 15, and 16, Plate XIII., the illumination of the fracture was obtained by indirect light from an arc lamp reflected on to the specimen from a cone of white paper fastened to the objective. Even with such diffusion the photographs do not satisfactorily represent all that can be seen by visual observation.

Fig. 14 shows the alternate bending fracture of a strip of Swedish iron in its normal state, viz. through irregular cleavages and with considerable deformation of the crystals before breaking. Fig. 15 shows the fracture of a specimen in which the crystalline boundaries had been rendered extremely brittle. None of the irregular little cleavage facets are present, but the surface is composed of the comparatively plane boundary surfaces of the polyhedral crystals existing in the mass. Fig. 16 shows a mixed fracture consisting mainly of rough cleavages, but in places plain facets representing boundary fractures are visible. To more thoroughly represent by photography the nature of the intercrystalline fractures, the device was tried of depositing an extremely thin coating of copper upon the fractured surface. If this is done from a bath of copper sulphate the bright reflecting surfaces of the crystals are somewhat dulled by the deposit and also by the slight etching. The brilliance of the fracture, such as seen in Fig. 15, is very much spoiled by the deposit, but Fig. 17, Plate XIV., which shows an intercrystalline fracture after about thirty seconds' immersion in copper sulphate solution, gives perhaps a rather better idea of the manner in which the crystals have broken away from one

another. In the further experiments described below, upon the production and removal of intercrystalline brittleness, microscopic examination of the fractured surfaces has been the principal means by which the nature of the specimens has been determined.

The production of brittleness by the presence of Mabor in the evacuated furnace was evidently due to gases which it gave off on heating, and not to some component of the material which remained solid,¹ for samples in the furnace entirely out of direct contact with it were just as much affected as those lying upon it. Experiments were therefore carried out to determine the nature of these gases. A slab of Mabor, weighing 18·4836 grammes, was heated *in vacuo* for about three hours at 1000° C., and the gases evolved collected over mercury and subsequently analysed. The total volume of gas collected was 28·13 cubic centimetres, and was found to contain over 98 per cent. of CO₂. The weight of this gas and that of the moisture contained in the Mabor (which was subsequently determined in another sample) roughly accounted for the loss of weight found after heating.

The evolution of CO₂, occurring on heating Mabor *in vacuo*, at once led to a series of experiments to determine whether the introduction of this gas in small quantities into a furnace in which samples of iron were heated *in vacuo* would have a similar effect upon the iron as the presence of Mabor. The results obtained entirely confirmed the view that it was indeed this gas which was responsible for both the etching of the samples and also for the production of intercrystalline weakness. Various experiments were carried out with different amounts of CO₂ added to the furnace before heating, and from these it was found that if the percentage of gas present was sufficient to form a complete coating of oxide upon the

¹ An analysis of the Mabor brick, kindly undertaken by Mr. W. Gemmell, gave the following results:—

	Per Cent.
Silicon	2·79
Ferric oxide	0·58
Alumina	0·59
Lime	16·42
Soda	1·23
Magnesia	78·39

outside of the samples, then these samples showed after annealing none of the signs of intercrystalline weakness which were found upon those annealed under conditions in which the surface still remained comparatively untarnished. Further experiments, in which some of the samples were given a previous coating of oxide by heating in air in a muffle, showed that this coating acted as a complete protection against the production of intercrystalline brittleness by annealing in a slight atmosphere of CO_2 ; such samples showing after treatment an entirely normal cleavage fracture, while other unoxidised samples annealed side by side with them broke readily along the crystalline boundaries when strained.

The vacuum usually obtained in furnace tubes used in the experiments was—unless very prolonged exhaustion was given before heating—never of an extremely high order, and therefore the tubes always contained a certain small proportion of oxidising gases. If the brittleness was, as appeared to be the case, due to the presence of small quantities of such gases, it would be expected that mere heating in such an incomplete vacuum should in time produce the same effect as the artificial addition of CO_2 . This result has been completely confirmed by experiment, and samples have been made extremely brittle by prolonged heating *in vacuo* alone, though the actual time of annealing to produce brittleness is longer than if more appreciable quantities of oxidising gases (but not such as to produce surface oxidation) are introduced.

In one experiment a sample of Swedish iron was annealed *in vacuo* for sixteen hours at about 1000°C . The strip after removal from the furnace showed a very completely developed intercrystalline fracture—so much so that a piece strained in tension broke off quite short along a path following a line of crystalline boundaries, with remarkably little deformation of the actual crystals themselves; the latter point being observed by the exceedingly faint development of slips bands upon the surface when viewed under the microscope. In all the brittle samples previously examined no indication could be seen under the microscope of any constituent existing in the boundaries of the crystals to which the brittleness could be ascribed; indeed, it was somewhat noticeable that considerable etching

was necessary to reveal the boundaries at all, and they then only appeared under the microscope as extremely fine lines, caused by the difference of level between adjacent crystals produced by etching. This fact is clearly seen in Figs. 10, 11 (Plate XI.), and 12 (Plate XII.). In the specimen mentioned above, however, subjected to sixteen hours' annealing *in vacuo*, it was found on repolishing and etching that in a few of the boundaries an apparently new constituent existed. Fig. 18, Plate XIV., shows a photomicrograph of this specimen, and it will be seen that a few isolated streaks of some body (appearing dark) exists along one of the crystalline boundaries. This substance only appeared in quite a small percentage of the boundaries, and never completely surrounding a crystal. On breaking the sample in tension the line of fracture did not specially follow the junctions in which it existed. It is doubtful, therefore, whether the brittleness can be directly ascribed to its presence.

EXPERIMENTS ON ANNEALING IN NITROGEN.

In all the experiments supplied above, the brittleness was produced by annealing at pressures far below that of the atmosphere; the amount of gases introduced into the exhausted furnace before heating, or those evolved from the iron itself, only being sufficient to raise the pressure some 10 centimetres in extreme cases. With the view of determining what part, if any, the low pressure played in producing the brittleness, a series of annealings were carried out in nitrogen at atmospheric pressure. The nitrogen used was obtained from a cylinder of compressed gas, and was not of absolute purity. The furnace tube was exhausted several times, and together with the pumps filled with nitrogen after each exhaustion, so that the air was very completely removed from the apparatus. After the final filling the furnace was kept in connection with the Sprengel pump, the fall tubes of which dipping below the surface of the mercury in the lower vessel, acted as non-return valves.

In the first experiment the nitrogen was passed over red-hot copper filings and through sulphuric acid before entering the furnace, and thus to a very great extent purified from any

oxygen and moisture. A strip of Swedish iron was annealed in the furnace for four hours at 1000°C . When afterwards tested it was found only to possess a very slight brittleness, the fracture only showing an occasional boundary surface. (The actual fracture is the one shown in Fig. 16, Plate XIII.).

In the second experiment the nitrogen was passed directly from the cylinder through sulphuric acid without passing over hot copper, and thus probably contained a small percentage of oxygen. The same annealing was given as before, and in this case a decidedly more brittle sample was obtained, but which still showed in places traces of cleavage fracture.

In the third experiment a few cubic centimetres of oxygen were added after filling the furnace with nitrogen, and a sample again heated for four hours at 1000°C . In this case complete intercrystalline brittleness was produced, the fracture of a sample exhibiting a complete series of boundary facets.

The last experiment was also repeated, using one clean strip of Swedish iron and one that had been given a coating of oxide by a previous heating in air. The result confirmed the fact previously obtained by annealing in a slight atmosphere of CO_2 , viz. that the oxide coating prevented that sample from becoming brittle. The clean sample showed, as before, a complete intercrystalline fracture, and broke if straightened after a slight bend, while the oxidised one only broke after several bends backwards and forwards and with the typical normal cleavage fracture.

REHEATING AND QUENCHING EXPERIMENTS.

Having obtained extreme intercrystalline brittleness in Swedish iron by annealing bright samples in a very slight oxidising atmosphere of oxygen or carbon dioxide, experiments were undertaken to see by what means the brittle material could be brought back into its normal condition. A preliminary trial of a sample rendered brittle by annealing on Mabor brick had shown that such a cure could be effected by re-annealing in hydrogen.

For the purpose of the reannealing experiments the special furnace, made by close winding Nichrome wire upon a silica

tube, was constructed, and is described in detail in the appendix. It was possible to heat small samples of metal in this furnace up to any desired temperature in a few minutes, and the temperature could be very quickly adjusted to within a few degrees. The results of the reheating and quenching experiments are given below in tabular form, the time of annealing being reckoned from the moment the desired temperature was attained until cutting off the heating current. The samples were in all cases broken by bending, and the nature of the fracture determined by low-power observation of the fractured surface. The quenching was done in the same furnace (see appendix), using water at 15° C. as the quenching liquid, and the sample was in all cases washed into the flask by the rush of water. A vacuum of a few millimetres of mercury was kept up in the furnace tube during heating.

*Reannealing and Quenching Experiments upon Swedish Iron
previously rendered Brittle.*

TREATMENT.	RESULT.
Heated for 1 hour in hydrogen at 1000° C.	Brittleness entirely cured.
Heated for 15 minutes in hydrogen at 1000° C.	Brittleness partially cured.
Heated for 1 hour in hydrogen at 820° C.	Brittle as before.
Heated for 1 hour in hydrogen at 700° C.	Do.
Heated for 1 hour in air at 1000° C.	Do.
Heated for 15 minutes in air at 1000° C.	Do.
Heated for 15 minutes at 1000° C. and quenched.	Brittleness cured.
Heated for 20 minutes at 820° C. and quenched.	Brittle as before.
Heated for 15 minutes at 1000° C., slowly cooled to 820° C., and quenched.	A few isolated boundary facets visible, but the bulk of the fracture cleavage.
Heated for 15 minutes at 1000° C., slowly cooled to 700° C., and quenched.	Brittleness partially cured, but fracture showed mainly boundary facets.
Sample cured by quenching from 1000° C., reheated at 820° C. for 1 hour.	Brittle as before.

The results of these experiments are further discussed below.

CONCLUSIONS.

The experimental data obtained in the course of the research may be summarised as follows ;—

(1) Intercrystalline brittleness is produced in a pure iron—which in its normal condition is stronger along the crystalline boundaries than across the cleavage planes of the individual crystals—by annealing above the Ar_1 point (670°C.) in an atmosphere containing a small amount of oxygen or carbon dioxide. The presence of an inert gas, such as nitrogen, sufficient to bring the total pressure up to that of the atmosphere does not prevent the production of the brittleness.

(2) Intercrystalline brittleness is not produced under similar conditions as regards temperature and time of annealing, if the oxidising gases are present in sufficient quantity to form a continuous coating of oxide upon the surface of the specimen; or if such a coating is previously formed upon the specimen by heating in the air, and it is then annealed under conditions which produce intense brittleness in clean specimens.

(3) Under given conditions of temperature and atmosphere the weakness of the intercrystalline joints becomes more marked as the period of annealing is prolonged. The brittleness is more readily produced if the temperature of annealing is above Ar_3 .

(4) The brittle samples may be completely restored to their original condition by—

(a) Heating above the Ar_3 change and quenching.

(b) Reannealing for a sufficient length of time in hydrogen above the Ar_3 change point.

(5) The brittle samples may be partially restored by—

(a) Heating above Ac_2 , cooling to between Ar_3 and Ar_2 , and quenching.

(b) Heating above Ac_3 , cooling to between Ar_2 and Ar_1 , and quenching. The restoration is less complete in (b) than (a).

(c) Short annealing in hydrogen above Ar_3 .

(6) The brittle samples are unaffected by—

(a) Heating to below Ar_3 and quenching.

(b) Reannealing in hydrogen below Ar_3 .

(c) Reannealing in air at temperatures up to 1000°C.

In explanation of these experimental data the author offers the theories contained in the following paragraphs:—

(1) That annealing samples of nearly pure iron in a slightly

oxidising atmosphere apparently results in the formation of an oxide of iron which is soluble in γ -iron, but insoluble or very much less soluble in α -iron. Owing to its insolubility in α -iron it is thrown out into the α crystalline boundaries when these are formed on cooling, and its presence there results in a lack of cohesion between the crystals, and the consequent production of intercrystalline brittleness.

(2) The amount of oxide passing into and out of solution is exceedingly small, and its presence in a continuous envelope is not revealed by the microscope, even in samples showing extreme brittleness. The surfaces of the crystals in a fracture also are bright, and show no visible traces of foreign matter

(3) The oxide is not one of those usually formed when the oxidising gases are present in some quantity, which oxides are apparently insoluble in all varieties of iron, and thus incapable of producing brittleness.

(4) A coating of oxide formed in a strongly oxidising atmosphere prevents the formation of the soluble oxide and hence prevents the metal from becoming brittle.

(5) The formation and solution of the soluble oxide are comparatively slow, due probably to the fact that they must be preceded by the removal or oxidisation of any hydrogen or carbon monoxide in solution in the iron. The removal of these gases from solution in the iron would probably be hastened by annealing *in vacuo*. These gases have been shown by Baker¹ to be evolved at a maximum rate from steel *in vacuo* at a temperature corresponding to the Ar_1 change, and it is above this temperature only that brittleness has been produced.

In considering these conclusions it is necessary to follow the changes which go on in the crystal structure of a sample of iron when it is heated and cooled through the change points, and concerning this we can deduce considerable information from the surface patterns which are produced on a polished sample during heating and cooling, and which have been described in connection with some of the vacuum annealing experiments. It was found on examining such a sample

¹ *Carnegie Research Memoirs: Journal of the Iron and Steel Institute*, No. I., 1909, pp. 219-226.

that if it had been heated above the Ar_3 point two distinct networks were visible, one of which represented the boundaries of the γ crystals of the iron, and the other the boundaries of the α crystals which remained when cold. The two networks crossed each other in a quite irregular manner, and generally the α network represented considerably larger individual crystals than the γ . If the sample had been heated below the Ar_3 point, only one network—representing the final α crystals—was visible. These facts show that the iron on passing through the Ar_3 change point undergoes a complete recrystallisation, the boundaries of the γ crystals above Ar_3 being entirely distinct from those of the α existing after this point had been passed. The change from β - to α -iron at Ar_2 is not accompanied by such alterations in the crystal formation. If any carbon is present in the iron it is known that at the Ac_1 change point a certain amount of α iron, sufficient to hold the carbide in solid solution, is transformed into the γ variety. This γ -iron would naturally be formed between the α crystal still remaining (since it is there that the pearlite is found), and would continue to grow into the α crystals until the complete change to γ at Ac_2 took place. On cooling, the reverse process takes place, a certain amount of γ solid solution remaining in the boundaries of the β or α crystals between Ar_3 and Ar_1 .

That the brittleness was due to the presence of an oxide seems evident from the conditions under which it is produced, and also from the two facts that it is cured by suitable reheating in hydrogen, but remains after a similar reheating in an oxidising atmosphere, such as air. That the oxide exists in a state of solution in the γ -iron is directly deduced from the quenching experiments, which show that quick cooling prevents the effects of its segregation in the boundaries when the α crystals are formed. Quenching between Ar_3 and Ar_1 partially cured the brittleness, showing that the segregation had started, but was not complete until below the Ar_1 change—that is, until all the γ -iron is transformed. It is not necessary to assume that the iron should contain any carbon, since it is probable that the presence of the oxide itself in solution would tend to retain a certain proportion of

the γ -iron as such below the Ar_3 change point. In this connection it may be recalled that Schenck has shown that an atmosphere of CO and CO_2 which reduces FeO may, especially at low pressures, oxidise cementite, and thus it is probable that some of the carbon, as well as the hydrogen and carbon monoxide, would be removed from the brittle samples before the oxide which causes the brittleness started to form. The solubility of this oxide in γ -iron is still further shown by the fact that the surface of samples heated over a temperature range was found to be unoxidised at all temperatures above Ar_1 , where presumably any oxide was dissolved as formed, but oxidised below this temperature where solution did not take place. The peculiar etching action on the α crystals between Ar_1 and Ar_2 may possibly be due to the mechanism of oxidation and solution in this region.

That the oxide causing the brittleness is only formed under the special conditions which also produce brittleness, viz. a small quantity of oxidising gases in the annealing atmosphere and a clean surface is clearly shown by the experiments, and it is naturally indirectly deduced from the known facts that in all the heating processes which iron undergoes during the course of manufacture (in practically every case accompanied by surface oxidation) no such brittleness is produced, such oxides, therefore, are not capable of solution.¹ The phenomenon may, however, have an important bearing upon the close annealing of iron and mild steel sheets, and it seems probable that many cases of failure under stamping, and the similar processes to which this class of material is subjected, can be ascribed to such causes. The fact that intercrystalline brittleness has been found in the transformer sheet (which material is always subjected to prolonged close annealing) seems decidedly to point to this conclusion.

It has been suggested by Ziegler² that any particles of foreign matter which are not in solution in γ -iron at the Ar_3 point act as nuclei upon which the α crystals commence to

¹ The author acknowledges as an objection to this theory that it is difficult to understand why the soluble sub-oxide should not always be formed by reaction between the iron and the usual oxide skin; he is unable to offer an explanation of why this reaction does not apparently take place.

² *Revue de Métallurgie, Mémoires*, vol. viii, pp. 655-672.

form on cooling, and are hence found in the centres and not in the boundaries of these crystals. An oxide therefore which did not pass into solution in the γ state would not be afterwards found in the α boundaries on cooling. Annealing the brittle samples in hydrogen below the Ar_3 did not cure the brittleness. From this it appears that *all* the oxide did not pass into solution between the Ac_1 and Ac_2 , and although such as was left would probably be reduced again to iron, yet the iron formed would not occupy the whole space left by the oxide, and hence a gap would remain and the lack of crystalline cohesion be as bad as, if not worse than, before.

The theory has been recently advanced by Bengough¹ that the normal strength of the intercrystalline boundaries in a metal is due to the presence of an amorphous cement, of a similar nature to Beilby's hard state produced by strain. The same theory has been independently given by Osmond,² and it was also suggested verbally to the author by Dr. Rosenhain³ before the publication of either of the former views. If such a view is correct, and to the author's mind the theory of crystal structure necessitates that it should be so, it must be assumed that any causes which prevent the formation of the amorphous film would necessarily lead to intercrystalline brittleness.

It thus seems probable that in samples of iron annealed under conditions producing intercrystalline weakness, the very small quantities of oxide which were rejected from the crystals on transforming, prevented the formation of the usual strong amorphous cement between the α crystals, and that it was especially due to the absence of any such binding material that the lack of intercrystalline cohesion must be ascribed. Bengough, in ascribing the remarkable changes in the

¹ "A Study of the Properties of Alloys at High Temperatures," read before the Institute of Metals, January 1911.

² Correspondence on Grenet's paper, *Journal of Iron and Steel Institute*, 1911, No. II. p. 62.

³ Dr. Rosenhain brought the idea forward as a suggestion that as the amorphous phase formed by polishing, &c., is known to be more readily soluble in acids than the crystalline phase, it might also possess a higher vapour pressure. It would thus volatilise to a greater extent on annealing *in vacuo*, and the crystal boundaries be weakened. The experiments have since shown that such an action does not account for all the phenomena observed.

mechanical properties of metals at high temperatures to the absence of the amorphous cement between the crystals, draws special attention to the "cry" given out by metals when strained above the "temperature of recuperation." He explains this phenomenon as due to the rubbing of the crystal surfaces against one another. It has been noted on page 90 that such a "cry" was always heard on straining samples of the author's brittle material.

In conclusion, the author wishes to express his thanks to the authorities of the National Physical Laboratory, and especially to Dr. Glazebrook, F.R.S., the Director, and to Dr. W. Rosenhain, the Superintendent of the Department of Metallurgy and Metallurgical Chemistry, for their permission to use the facilities of the Laboratory for carrying out the research. Dr. Rosenhain has taken a personal interest in the work, and the author is indebted to him for many valuable suggestions.

APPENDIX.

APPARATUS EMPLOYED IN THE EXPERIMENTAL WORK.

Furnace for Prolonged Annealing "in vacuo."

A sketch of this furnace is shown in Fig. 1. "A" is a silica tube 10 inches long and 1 inch internal diameter wound externally with a heating coil of Nichrome wire. The winding was laid on non-inductively by bending the wire through 180° after winding one spiral and then returning backwards to the start by a second spiral lying midway between the coils of the first. A layer of asbestos paper was placed between the two windings to prevent accidental shorting, and a special insulation of asbestos string wound round the last turn and lead of the outside spiral to prevent direct shorting at the end where both leads emerged. The tube was enclosed in a uralite box, and packed with magnesia.

"B" is a tube of glazed Berlin porcelain, $\frac{5}{8}$ inch internal diameter, fitting loosely into the silica tube and projecting about 5 inches at either end. One end of this tube was closed by a rubber bung through which passed a glass tube leading to the air pump, and the other by a similar bung, through which passed the tube of a glass tap for admitting gases to the sample. If it was not required to admit gases during the annealing, the bung was replaced by a glass window (fastened by means of a thick solution of sealing-wax), through which the temperature of the sample could be measured with an optical pyrometer. It was found that if thermo-couples were used in the exhausted tube with

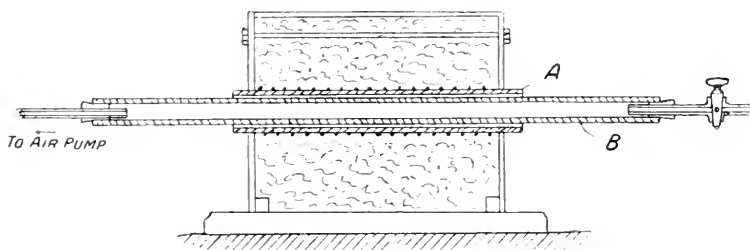


FIG. 1.—Vacuum Annealing Furnace.

the iron they very quickly became brittle; and thus the temperature of annealing was either measured optically or by inserting the couple between the silica and porcelain tubes. The failure of the thermo-couples may be ascribed either to reducing gases giving off from the iron on heating, or possibly to similar causes which produced the brittleness in the iron itself. The porcelain tube was exhausted by means of a three-fall Sprengel pump fitted with an automatic mercury lift worked from a filter pump; and the exhaustion could thus, if required, be carried on continuously throughout the experiment.

Furnace for Melting Iron "in vacuo."

This is shown in Fig. 2. "A" is a glazed porcelain tube, $1\frac{1}{2}$ inches internal diameter and 26 inches long, with 12 inches in the centre wound with a spiral of Nichrome wire and heat

insulated with a uralite casing packed with magnesia. The

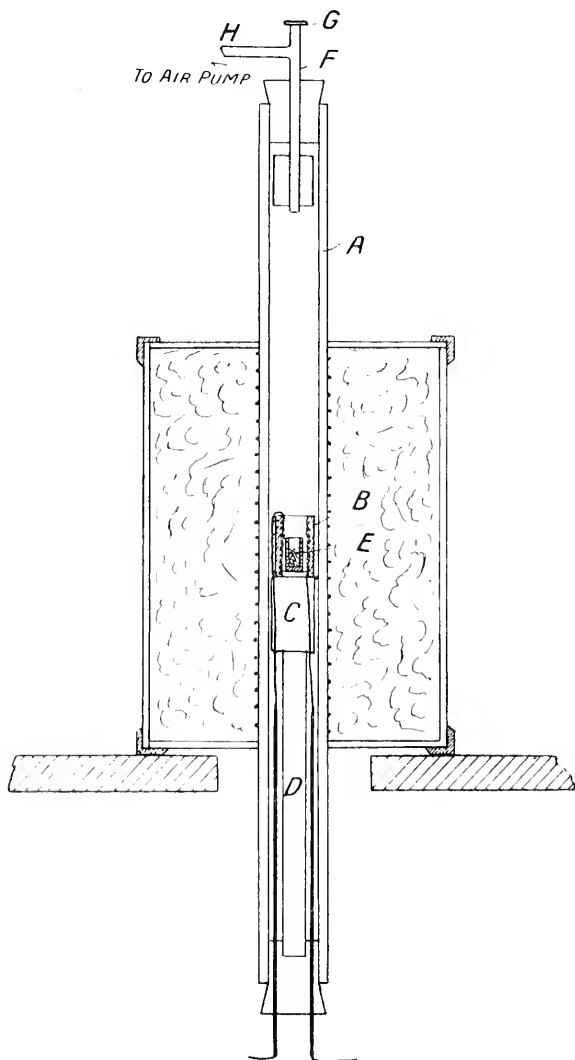


FIG. 2.—Vacuum Melting Furnace.

tube was supported vertically in use,¹ and by means of the

¹ This furnace was also used for vacuum annealing large samples, using the external winding only, and supporting with the tube horizontal.

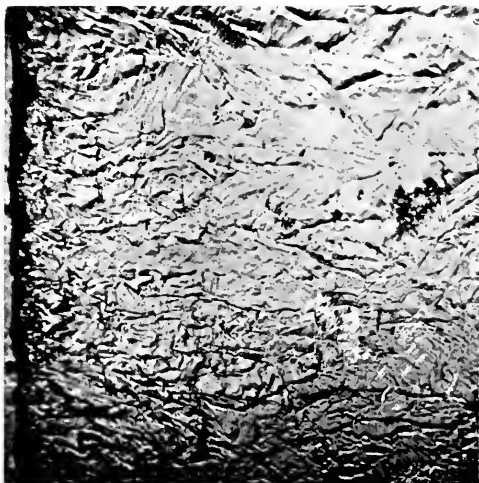


FIG. 1.—Electrolytic Iron as deposited. Structure near Cathode. Magnified 800 diameters and slightly reduced.



FIG. 2.—Electrolytic Iron as deposited. Structure near Outside. Magnified 800 diameters and slightly reduced.



FIG. 3.—Electrolytic Iron Sheet showing Fracture along Boundaries of Large Crystals. Magnified 2 diameters and slightly reduced.



FIG. 4.—Surface of Transformer Sheet after annealing *in vacuo* upon a "Mabor" Slab. Magnified 1000 diameters and slightly reduced.



FIG. 5.—Intercrystalline Fracture of Transformer Sheet. Magnified 800 diameters and slightly reduced.



FIG. 6.—Surface of Swedish Iron after heating *in vacuo*. γ Region.
Magnified 300 diameters and slightly reduced.



FIG. 7.—Same specimen as Fig. 6. β Region.
Magnified 300 diameters and slightly reduced.



FIG. 8.—Same specimen as Fig. 6. *a* Region.
Magnified 300 diameters and slightly reduced.

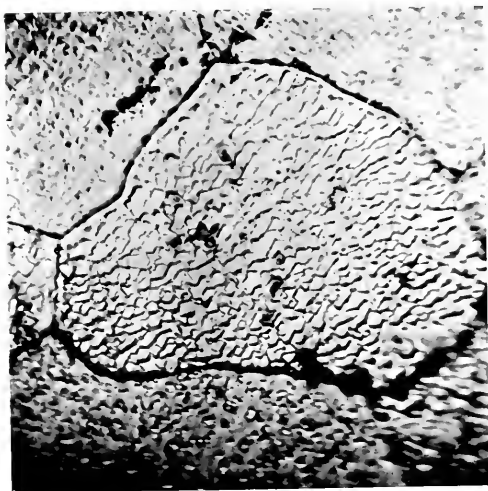


FIG. 9.—Part of Fig. 8.
Magnified 800 diameters and slightly reduced.



FIG. 10.—Fracture in Region corresponding to Fig. 6.
Magnified 150 diameters and slightly reduced.

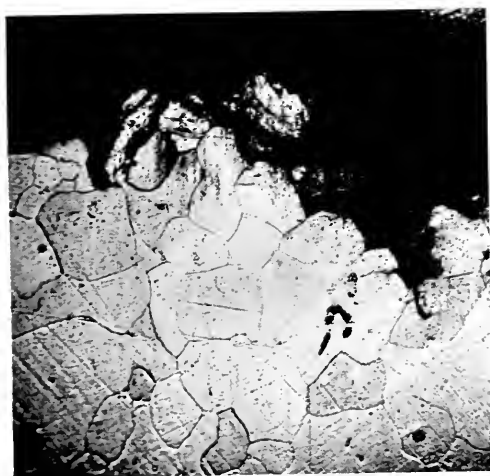


FIG. 11.—Fracture in Region corresponding to Fig. 7.
Magnified 150 diameters and slightly reduced.



FIG. 12.—Fracture in Region corresponding to Fig. 8.
Magnified 150 diameters and slightly reduced.



FIG. 13.—Cleavage Fracture in part of Specimen below A_1 .
Magnified 150 diameters and slightly reduced.



FIG. 14.—Cleavage Fracture of Swedish Iron. Magnified 30 diameters.

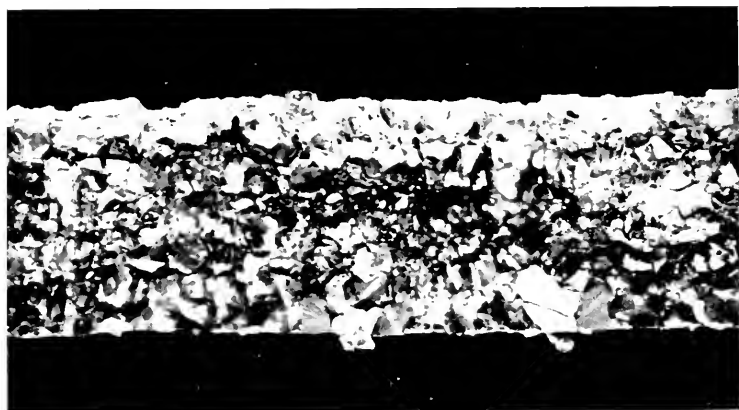


FIG. 15.—Intercrystalline Fracture of Swedish Iron. Magnified 30 diameters.



FIG. 16.—Mixed Fracture of Swedish Iron. Magnified 30 diameters.



FIG. 17.—Intercrystalline Fracture of Swedish Iron.
Etched with Copper Sulphate. Magnified 30 diameters.

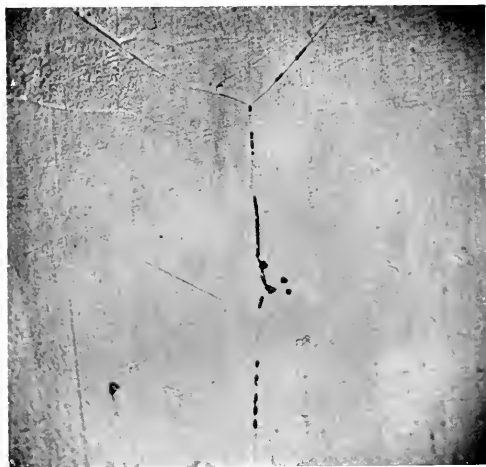


FIG. 18.—Swedish Iron after annealing 16 hours *in vacuo*.
Magnified 750 diameters and slightly reduced.

external winding could be heated in its central portion to a temperature of about 1000°C . To obtain the further 500° – 600°C . necessary to melt the iron, a secondary furnace "B" was supported in the centre of the tube upon a circular block of Mabor brick "C," which in turn was carried on a porcelain tube "D," resting upon the rubber bung closing the lower end of the outer tube. The furnace "B" consisted of a short tube turned in the lathe from Mabor brick, and having an internal screw thread, in the grooves of which was wound a spiral of platinum-rhodium wire 0.5 millimetre diameter. The small crucible "E," containing the "ferrum reductum" powder to be melted, was also turned out of Mabor, and fitted loosely inside the secondary furnace. The leads from the platinum-rhodium winding were joined to stout nickel wires passing through the rubber bung at the bottom of the outer tube. The whole of the secondary furnace, crucible, supports, &c., were built up upon the bung before inserting into the outer furnace tube.

The upper end of the porcelain tube was also closed by a rubber bung, through which passed a glass tube "F," terminating in a window "G," and having a second tube "H" teed into it and connected to the air-pump. A direct view of the material in the crucible could be obtained through "G," and its temperature measured by an optical pyrometer. A further block of Mabor, with a hole drilled through its centre, was supported just below the upper bung to prevent the latter from being scorched by radiation. The furnace was exhausted by means of a powerful mechanical mercury pump capable of sustaining a high vacuum within it. The author would like to express his thanks to Dr. J. A. Harker, F.R.S., for his advice in constructing this furnace.

Furnace used for Reheating and Quenching Experiments.

This consisted of a length of silica tubing, $\frac{1}{2}$ inch internal diameter, wound for about three inches of its length with a close spiral of Nichrome wire. This wire, as supplied, is coated with a thin layer of oxide, and the author has found that this oxide is sufficient to insulate consecutive coils from

one another, so that they may be wound in actual contact. In order to have very small heat capacity no covering was placed over the winding, and it was found that the temperature in the tube would follow within a few seconds any alteration in the current passing through the winding. By the manipulation of an external resistance any desired rate of heating

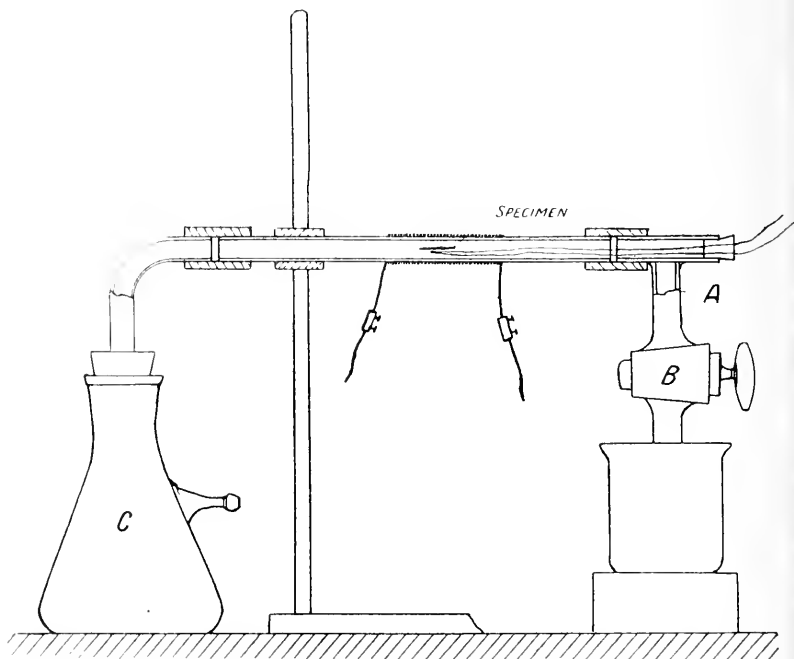


FIG. 3.—Quenching Furnace.

or cooling could be obtained, and the temperature adjusted quickly to any desired value.

For the quenching experiments this furnace was fitted as shown in Fig. 3, with arrangements similar to the Rosenhain quenching furnace in use at the National Physical Laboratory. To one end was attached, by means of a rubber tube, a glass tube of equal internal diameter to the silica, and from this tube descended a T-piece (A), furnished with a large bore glass tap (B). The further end of the glass tube was closed

by a rubber bung, through which passed the wires of a thermocouple by which the temperatures of the specimens were measured. Another glass tube was attached to the other end of the furnace tube and passed through the bung of a filter flask (C) connected to the air-pump. When it was desired to quench the specimen, a beaker of water was placed under the tube (A) and the tap opened. The rush of water carried the specimen right through into the flask and rapidly quenched it.

THE PRODUCTION OF STEELS AND FERRO - ALLOYS DIRECTLY FROM ORE IN THE ELECTRIC FURNACE.¹

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INTRODUCTION.

A review of previously published literature on the production of steels and ferro-alloys directly from ore in the electric furnace, and the report of the author concerning experimental work performed by him on this subject, are presented according to the following outline :—

PART I.

HISTORICAL DATA.

The production of steel directly from ore.

The production of steel directly from ore in the electric furnace.

The production of alloy steels directly from ore in the electric furnace.

Molybdenum steels.

Tungsten steels.

The production of ferro-alloys directly from ore in the electric furnace.

Ferro-chromium.

Ferro-molybdenum.

Ferro-tungsten.

PART II.

RESEARCH UPON THE PRODUCTION OF STEELS AND FERRO-ALLOYS DIRECTLY FROM ORES IN THE ELECTRIC FURNACE.

Experimental furnaces.

Apparatus and instruments.

¹ Received March 13, 1912.

The production of steels directly from ore in the electric furnace.

Theoretical considerations.

Experiments.

Discussion of results.

Steels.

Slags.

Operation of the furnace.

Electrodes.

Percentage extraction.

Energy consumption.

A continuous process for the production of steels directly from ore in the electric furnace.

Cost.

Conclusions.

The production of chromium steel directly from ore in the electric furnace.

Experiments.

Conclusions.

The production of molybdenum steel directly from ore in the electric furnace.

Experiments.

Conclusions.

The production of tungsten steel directly from ore in the electric furnace.

Experiments.

Conclusions.

The production of ferro-chromium directly from ore in the electric furnace.

Experiments.

Conclusions.

The production of ferro-molybdenum directly from ore in the electric furnace.

Experiments.

Conclusions.

The production of ferro-tungsten directly from ore in the electric furnace.

Experiments.

Conclusions.

The author expresses deep appreciation for the assistance rendered him in the performance of the research by Dr. Frank W. Traphagen, Mr. William G. Haldane, and Mr. Edward J. Dittus of the Metallurgical Department of the Colorado School of Mines, Mr. J. Barnaby Conrad, the officials of the Colorado Fuel and Iron Company, who kindly supplied some of the raw materials, and others.

PART I.

HISTORICAL DATA.

THE PRODUCTION OF STEEL DIRECTLY FROM ORE.

For many years steel and wrought iron have been produced directly from ore on a small scale in the forge, crucible, and reverberatory furnace; but the difficulties attending the operation of the processes in an economic manner on a large commercial scale have prevented their adoption to any great extent. At the present time it is only in remote regions that steels and malleable irons are made directly from ores.

The advent of the electric furnace has somewhat renewed the interest of metallurgists in direct processes for the manufacture of steel. This is due to the great possibilities for the removal of impurities in the slag at the high temperature attainable in the electric furnace, and the closer regulation of the carbon content of the product.

Steel¹ was reduced directly from hæmatite and magnetite ores in small fireclay crucibles in India 2000 years ago, giving as a product Wootz steel. Other processes used at intervals during the past centuries are the native forge or bloomery process, puddling processes, the Catalan process, the American bloomery process, and the high bloomery or continuous process. Chenot reduced iron ore in retorts with direct heating by charcoal, or indirect heating by producer-gas. Eames used a reverberatory furnace fired with natural gas, and reduced the ore with coke or anthracite.

In 1878 Siemens patented a process for the direct production of steel and wrought iron from ore in a rotative regenerative furnace, using bituminous coal as a reducing agent. Experiments² were conducted several years ago in Lower Austria based upon the process of Särnström, introduced in 1882, and some later work of Husgavel, in which a soft steel was produced in an improved bloomery furnace resembling

¹ *Stahl und Eisen*, vol. xxi. (1901), pp. 209, 277, 337, 391.

² *Berg- und Hüttenmännisches Jahrbuch der k.k. Bergakademien zu Leoben*, vol. i. p. 1.

a small blast-furnace. Charcoal and coal-dust were used as a fuel. The product was soft and ductile, and was of the following composition: carbon, 0.16 per cent.; manganese, 0.06 per cent.; silicon, 0.095 per cent.; phosphorus, 0.024 per cent.; and sulphur, 0.014 per cent. Heskett¹ and Moore have recently invented a process for the manufacture of wrought iron and steel directly from ore by roasting and smelting with reducing gases. Other processes have been devised in which use is made of petroleum as a fuel in a modified blast-furnace.

In 1906 H. W. Lash² patented a process which consists of making an intimate mixture of ore, cast iron, and carbon, and submitting this mixture to heat, when, if the proportions of the constituents of the mixture have been properly adjusted, the desired grade of steel is produced. The essential features of the process seem to be the fine state of division of the constituents of the mixture, their intimate association, and the use of iron containing metalloids in considerable quantities. The cast iron is in the form of borings and is supposed to act as a carrier of oxygen, the metalloids contained also acting as reducing agents. The Lash process has been carried out on a very large scale in the open-hearth furnace. Hundreds of tons of steel have been made in this manner. Two-thirds of the steel bath is produced directly from the ore while the other one-third is produced from the granulated pig iron mixed with the ore. The advantages claimed for this process are: first, that a superior quality of steel is obtained in this way; second, that the cost of producing the steel is in general lower than when the regular methods are employed.

THE PRODUCTION OF STEEL DIRECTLY FROM IRON ORE IN THE ELECTRIC FURNACE.

The direct production of steel from iron ores in the electric furnace is still in the experimental stage. Just as pig iron can be produced from iron ore, so can malleable iron and steel be produced by a close regulation of the carbon content of the

¹ *Hüttenmännisches Rundschau*, 1906, p. 61.

² *Transactions of the American Electrochemical Society*, vol. xiv. (1908),^{*} p. 239; vol. xv. (1909), p. 149.

charge. Enough carbon is provided for the reduction of the ore, but not enough to combine to any appreciable extent with the product. This cannot be done in the blast-furnace because of the excess carbon which is present for fuel. The ore is reduced to pure iron, but this combines at once with any free carbon present. In the electric furnace the electrical energy does the heating while the carbon simply performs the chemical function of reduction. The reduction of the ore to steel is simple, but difficulty has been experienced in preventing a high loss of iron in the slag due to the low carbon content of the charge. The commercial success of a process of direct reduction in the electric furnace is yet to be determined by operations conducted on a large scale.

Experiments of Stassano.—Stassano¹ has performed two series of experiments in Italy on the direct reduction of steel from iron ore from the electric furnace, the first during the years 1898 to 1902, and the second in 1908. The first experiments were conducted in a modified blast-furnace in which electrodes were substituted for tuyeres. This furnace was unsuccessful, and the experiments of this series were completed in a hearth furnace similar to the modern Stassano furnace.

In the experiments of 1898 a first-class haematite ore was used, which was first crushed and then briquetted with charcoal, lime, and tar.

TABLE I.—*First Experiments of Stassano: Raw Materials.*

ORE.						Per Cent.
Fe ₂ O ₃	93.02
MnO	0.619
SiO ₂	2.79
CaO and MgO	0.50
Sulphur	0.058
Phosphorus	0.058
Moisture	1.72
LIMESTONE.						
CaO	51.21
MgO	3.11
SiO ₂	0.90
Al ₂ O ₃ and Fe ₂ O ₃	0.50
CO ₂	43.43

¹ *Electrochemical and Metallurgical Industry*, vol. vi. (1908), p. 315; *Ibid.* (1906), pp. 125, 152, 265, 332; *Journal of the Iron and Steel Institute*, 1911, No. 11.; *Metallurgical and Chemical Engineering*, vol. ix. (1911), p. 642.

CHARCOAL.						Per Cent.
Carbon	90.42
Ash	3.88
Moisture	5.70
TAR.						
Carbon	59.20
Hydrocarbons	40.50
Ash	0.27

TABLE II.—*First Experiments of Stassano: Charges.*

Charge.	I.	II.	III.	IV.	V.	Parts by Weight.
	Kg.	Kg.	Kg.	Kg.	Kg.	
Iron ore	43.68	35.26	40.60	40.43	50.15	1000
Limestone	5.45	4.41	5.07	5.06	6.27	125
Charcoal	6.98	5.63	6.50	6.47	8.03	160
Tar	5.26	4.23	4.88	4.86	6.00	120
Total	61.37	49.54	57.05	56.82	70.45	...

TABLE III.—*First Experiments of Stassano: Products.*

	I.	II.	III.	IV.	V.	Average.
	p. Cent.	p. Cent.	p. Cent.	p. Cent.	p. Cent.	
Carbon	0.120	0.092	0.113	0.091	0.090	...
Manganese	0.106	0.095	0.109	0.083	0.092	...
Silicon	0.048	0.022	0.028	trace	trace	...
Phosphorus	0.0055	0.024	0.013	0.0016	0.009	...
Sulphur	0.073	0.062	0.046	0.065	0.059	...
Weight, kilogrammes	26.05	22.05	22.05	24.78	30.70	...
Kilowatt-hours per kilogramme	4.34	5.20	4.91	3.56	3.08	4.21
Kilowatt-years per ton	0.49	0.59	0.56	0.41	0.35	0.48
Efficiency	45.56	37.07	41.11	55.02	61.33	48.01

The total production of steel during the experiments was 125.63 kilogrammes, and Stassano estimates the electrode consumption at 12 kilogrammes per ton¹ of steel produced.

The first experiments of Stassano demonstrated that malleable iron or a fluid steel could be produced directly from a very pure ore in the electric furnace, but showed nothing of the possibilities of the process with ores high in phosphorus and sulphur. The power consumption was so high, and the cost of briquetting the ore so great, as to prevent the commercial application of the process. Stassano at the conclusion

¹ The metric ton is used throughout this report.

of the first experiments estimated the cost of production of 1 ton of steel by this process as \$27.62.

In the second series of experiments four charges were worked on an ore of poorer quality than that first used. The ore was crushed and briquetted with a 25 per cent. solution of sodium silicate as a binder. The experiments were conducted in a 150-kilowatt three-phase furnace.

TABLE IV.—*Second Experiments of Stassano.*

ORE.						Per Cent.
Fe ₂ O ₃	68.70
Mn ₃ O ₄	3.23
SiO ₂	17.15
Al ₂ O ₃	2.00
CaO	1.00
MgO	5.67
Phosphorus	0.15
Silicon	0.12

CHARGES.						Kilogrammes.
Ore	100
Limestone	35
Charcoal	24
Sodium silicate	8
Calcium carbonate	5

PRODUCTS.						
	I.	II.	III.*	IV.*	Average.	
	Per Cent.	Per Cent.	Per Cent.	Per Cent.		
Carbon	0.25	0.26	0.30	0.80	...	
Manganese	0.12	0.21	0.24	0.30	...	
Silicon	0.07	0.03	0.14	0.22	...	
Phosphorus	0.010	0.10	0.015	0.015	...	
Sulphur	0.065	0.040	0.07	0.045	...	
Kilowatt-hours per kilog.	4.5	4.3	4.0	4.2	4.25	
Kilowatt-years per ton	0.51	0.49	0.46	0.48	0.48	

* Pig iron added for recarburisation after the removal of slag. In Experiment No. III. calcium carbide was added after the removal of slag.

The second series of experiments show the possibility of obtaining a steel of good quality from ore containing impurities, but, as in the first experiments, the power consumption was very high, and the briquetting of the charge was considered necessary.

Investigations of J. W. Evans.—In 1906 J. W. Evans¹ of Canada performed experiments on the direct smelting of ores and the production of steels from sulphurous and titaniferous ores. The work was done in a small electric crucible furnace holding about an ounce of charge. From an ore containing 68.01 per cent. iron and 1.01 per cent. sulphur, three products were made of the following composition: (1) carbon, 0.05 per cent.; silicon, 0.01 per cent.; sulphur, 0.12 per cent.; (2) carbon, 0.07 per cent.; silicon, trace; sulphur, 0.17 per cent.; and (3) carbon, 0.06 per cent.; silicon, 0.04 per cent.; sulphur, 0.08 per cent. With a titaniferous iron ore containing 45.17 per cent. iron and 7.44 per cent. titanium, products of the following percentage composition were obtained: (1) carbon, 0.51 per cent.; silicon, 0.62 per cent.; titanium, 0.37 per cent.; (2) carbon, 0.84 per cent.; silicon, 2.31 per cent.; titanium, 1.02 per cent.; and (3) carbon, 0.87 per cent.; silicon, 0.05 per cent.; no titanium. Evans states that the titanium passed into the slag regularly with a high-line content of the charge. If the titanium is retained in the metal by making the slag more acid, a large part of the silicon also passes into the metal.

In 1910 the results² of later work were published by Evans on the production of a tool steel directly from ore. The experiments were performed in a small shaft furnace of about 5 kilogrammes capacity. The furnace had two lateral electrodes between which an arc was formed. A magnetite ore was used of the following percentage composition: iron, 51.45 per cent.; titanium, 7.50 per cent.; sulphur, trace; nickel, 0.12 per cent.; vanadium, trace. The ore was crushed and briquetted with charcoal and limestone, molasses and water being used as a binding material. The charge was 2833 grammes of ore, 566 grammes of limestone, 510 grammes of charcoal, 283 grammes of molasses, and 453 grammes of water. From this charge about 2 kilogrammes of metal of the following percentage composition was produced: carbon, 1.25 per cent.; silicon, 1.06 per cent.; sulphur, 0.124 per cent.; phosphorus, 0.051 per cent.; no titanium, no vanadium. The high per-

¹ *Journal of the Canadian Mining Institute*, vol. ix. p. 128.

² *Ibid.*, vol. xiii. p. 151.

centage of sulphur in the steel was caused by some calcium sulphate which contaminated the lining. The conclusions drawn are, that 1 kilogramme of tool steel reduced in a small electric furnace would require 6.6 kilowatt-hours per kilogramme. With a large furnace producing 1 ton or more per 24 hours, A. Stansfield estimates the power consumption to be 4.4 kilowatt-hours per kilogramme of steel, or 0.50 kilowatt-years per metric ton. The electrode consumption is estimated at 66 kilogrammes per metric ton. With power at \$26.80 per kilowatt-year the cost of production is estimated at \$44.00 per metric ton.

Investigations of W. G. Brown and F. E. Lathe.—To determine the possibility of obtaining steel free from sulphur and phosphorus in a continuous smelting furnace, experiments were conducted in 1907 by W. G. Brown and F. E. Lathe, under the direction of Dr. A. Stansfield of McGill University. The furnace used was similar to the experimental furnace used at Sault Ste. Marie, but as a low carbon steel was to be made, the carbon crucible of the latter furnace was replaced by a lining of dead burned magnesite, and lower electrode connections were made by means of an iron rod passing through the bottom of the furnace. The furnace was operated continuously for several hours at a time, and low carbon steel tapped in 1 or 2 kilogramme quantities every half hour.

A pure Lake Superior hæmatite ore which contained 61.8 per cent. iron was charged. A flux of sand and lime was used so as to make a slag equal to about half the weight of the metal produced. One per cent. each of sulphur and phosphorus was added as monosulphide of iron and calcium phosphate to make the ore impure.

A study of Table V. shows that as the carbon content is decreased in the charge the silicon and phosphorus are decreased in the steel, but the percentage of sulphur is not affected. The investigators state that the sulphur was not reduced, as would have been the case in the production of pig iron, because with the decrease in carbon the smelting conditions become less favourable for the formation of calcium sulphide. However, with the change to an oxidising slag a portion of the sulphur was probably removed as calcium sul-

plate, as in the basic open-hearth process. Also, it appears that if an attempt was made to reduce the carbon in the steel by lowering the amount of carbon charge, the percentage of iron oxide in the charge was largely increased without a corresponding reduction of carbon in the steel. Hence, it may be concluded that difficulty may be experienced in the elimination of sulphur from the steel in a direct electrothermic process performed in a continuous furnace, although this may be accomplished in an intermittent furnace, and that phosphorus can be slagged when a low carbon steel is produced.

TABLE V.—*Investigations of Brown and Lathé.*

	I.	II.	III.	IV.	V.	VI.	VII.
	p. Cent.	p. Cent.	p. Cent.	p. Cent.	p. Cent.	p. Cent.	p. Cent.
Steel—							
Carbon . . .	2.09	1.16	0.54	0.088	0.088	0.091	0.088
Silicon . . .	0.20	0.15	0.24	trace	trace	trace	trace
Sulphur . . .	0.75	0.91	1.04	0.54	0.65	0.47	0.68
Phosphorus . .	0.49	0.24	0.20	0.039	0.048	0.031	0.081
Slag—							
FeO	4.5	7.1	3.6	20.54	20.64	26.94	33.46
SiO ₂	31.7	30.3	32.2	16.77	18.92	15.66	15.42
CaO	30.7	30.8	36.0	27.07	35.17	35.17	32.54
MgO	15.8	21.3	17.6	22.34	13.90	13.84	11.34
Al ₂ O ₃	13.2	9.3	11.7	7.48	5.30	3.53	2.13

*Experiments of "La Neo-Métallurgie."*¹—Experimental work on a commercial scale has been recently performed on the production of steel directly from ore in the electric furnace at the plant of "La Neo-Métallurgie." This work was done by Neveu and Arnou under the direction of Rémond and Chaplet. The results of these experiments are the most recent to be published.

Iron and steel of all grades were obtained from any kind of iron ore, under any physical conditions, and of any carbon content. The experiments have been on a large scale, and have given way to actual manufacture. More than fifteen tons of metal have been produced. An arc furnace of the intermittent type was used for the experiments. In a normal run the slag contains less than 8 per cent. of ferrous oxide, and it has often been possible to make a white slag by the use of additional reducing agents.

¹ *Revue de Métallurgie*, December 1910, p. 1190.

In order to carry on the reduction under the best conditions possible, briquettes of hæmatite and carbon were charged in the first experiments. Charcoal previously crushed and dried was also used. Then, in order to reduce the cost of the operation, briquettes of hæmatite alone were tried, thus charging a mixture of dried hæmatite briquettes and charcoal. Then the use of finely-crushed carbon and ore was tried. The results were identical with those of the first experiments, both from the view point of the composition of the product and the precision and regularity of the operations. The production varied slightly in the three cases, and for the same amount of power was: with briquettes of ore and carbon, 35 kilogrammes per hour; with briquettes of ore, 32 kilogrammes per hour; and with powdered ore and carbon, 31 kilogrammes per hour. From these results it is evident that it is not difficult to reduce pulverant minerals in the electric furnace. Finely-powdered carbon can also be used. Direct reduction in lumps is no more difficult.

TABLE VI.—*Composition of the Raw Materials.*

	Fe ₂ O ₃ per Cent.	Fe ₃ O ₄ per Cent.	FeCO ₃ per Cent.	SiO ₂ per Cent.	CaO per Cent.	Al ₂ O ₃ per Cent.	S per Cent.	P per Cent.	Mn per Cent.
Hæmatite . . .	93·82	3·57	0·33	0·78	0·023	0·052	trace
Magnetite	95·84	...	0·60	0·20	0·60	0·40	0·03	0·10
Siderite	80·80	8·96	1·00	0·75	0·04	0·02	2·98

	Fixed Carbon per Cent.	Volatile Matter per Cent.	Ash per Cent.	Sulphur per Cent.
Coke	92·55	6·25	0·90	0·125
Charcoal	88·02	10·54	1·35	...
Anthracite . . .	83·20	...	5·35	1·32

Any mineral could be easily reduced regardless of the form of carbon used. With charcoal the voltage has a tendency to stay higher than with coke or anthracite, but in an intermittent operation which does not demand the use of high incandescent

columns, these differences are of no importance, as the electrical characteristics of a run can be regulated at will by varying the height of the electrode.

TABLE VII.—*Analyses of Seven Consecutive Runs.**Soft Steel.*

Carbon per Cent.	Manganese per Cent.	Silicon per Cent.	Sulphur per Cent.	Phosphorus per Cent.
0·08	0·10	0·02	0·02	trace
0·09	0·09	0·04	0·02	"
0·11	0·46	0·06	0·02	" ferro-manganese added
0·09	0·15	0·08	0·02	"
0·10	0·12	0·07	0·02	"
0·13	0·10	0·03	0·02	"
0·10	0·14	0·19	0·012	"
<i>Hard Steel.</i>				
1·25	0·25	...	0·016	...
0·28	0·12	...	0·10	...
0·14	0·41	...	0·16	...

These results were all obtained directly without a single refining operation or the use of a slag, which would have lowered the sulphur content of the metal. The first furnace used in these experiments did not permit discharges. For this reason complete elimination of the sulphur from the steel was impossible, because the slags could not be changed.

Direct current and alternating current gave the same results. There was no electrolytic action. To determine this the poles were changed when direct current was being used. A furnace of 120 kilowatts capacity was used in most of the experiments. In a single operation for the reduction of hæmatite with charcoal and the production of soft iron, the energy consumed will vary from 3430 kilowatt-hours with a 120-kilowatt furnace to 2600 kilowatt-hours per metric ton with a 200-kilowatt metric furnace. With a very large furnace less than 2500 kilowatt-hours per ton of steel should be necessary.

With a plant close to a mine delivering magnetite with 66 to 68 per cent. iron for \$3·00 per ton, with power at 0·12 cents per kilowatt-hour and charcoal at \$12·00 per ton, the cost of producing a metric ton of steel is estimated at \$18·34.

With anthracite available at a cost of \$5.00 per ton, and rich hæmatite at \$5.00 per ton, if power costs 0.12 cents per kilowatt-hour, the cost of producing a ton of steel is estimated at \$19.44; at 0.4 cents per kilowatt-hour, \$26.72, and at 0.7 cents per kilowatt-hour, \$34.52. These figures of cost of production are probably low, because in the calculations apparently no consideration was taken of capital charges and depreciation.

TABLE VIII.—*Energy Consumption per Ton of Steel :
120-kilowatt Furnace.*

	Kilowatt- years.	Kilowatt- hours.
Magnetite and charcoal . . .	0.36	3150
„ „ anthracite . . .	0.35	3050
Hæmatite „ charcoal . . .	0.39	3430
„ „ anthracite . . .	0.35	3100
Siderite „ anthracite . . .	0.46	4000

The Application of the Lash Process to the Electric Furnace.—Experiments¹ were conducted at Niagara Falls on the application of the Lash process to the electric furnace in a 3-ton Héroult furnace by Fitzgerald and Bennie. Twenty-six runs were made under variable conditions. It was found possible to accomplish complete reduction of the charge with an expenditure of 0.205 kilowatt-years per ton of steel, and to turn out a finished product with an energy consumption of 0.247 kilowatt-years per ton. It is believed that under suitable conditions the power consumption would not exceed 0.188 kilowatt-years per ton. The electrode consumption was high in many of the runs. The best result obtained in the experiments was 31.3 kilogrammes per ton of steel cast, but it is believed that this may be reduced to 22.7 kilogrammes per ton.

About 50 tons of steel were manufactured of all grades from high carbon tool steel to metal running below 0.10 per cent. carbon, the yield of metal amounting to 98 per cent. in the preliminary experiments, although in some cases the slag

¹ *Transactions of the American Electrochemical Society*, vol. xiv. (1908), p. 239; vol. xv. (1909), p. 149.

contained as high as 15 per cent. iron; in the later runs it carried 6 per cent. iron. In the small furnace the slag loss was from 0.3 to 0.6 per cent. of the total iron in the mixture.

TABLE IX.—*Application of the Lash Process to the Electric Furnace.*

Raw Materials.	Lash Mixture.	Iron.	Heat No.			
			IX.	XI.	XXIII.	XXVII.
	p. Cent.	p. Cent.	p. Cent.	p. Cent.	p. Cent.	p. Cent.
Pig-iron . .	23	21.9	0.10	0.08	0.02	0.22
Ore	60	39.0	0.75	0.09	0.41	0.94
Coke	11	...	0.015	0.015	0.038	0.033
Lime	6	...	0.070	0.007	0.026	0.056
Total . . .	100	60.9	0.02	0.09	0.13	0.03
			Carbon . .			
			Manganese .			
			Phosphorus .			
			Sulphur . .			
			Silicon . . .			

Previous Research of the Author.—In 1910 the author¹ performed some experiments on the production of steel directly from ore in the electric furnace. The work was done in a small furnace holding about 2 kilogrammes of charge and of 5 kilowatts capacity. This furnace consisted of a crucible with a bottom-electrode of iron, imbedded in magnesite and a graphite upper-electrode. Alternating current was used.

TABLE X.—*Production of Steel directly from Ore.*

HEMATITE.		Per Cent.
Fe ₂ O ₃		94.90
SiO ₂		4.10
CaO		0.79
Al ₂ O ₃		1.46
Phosphorus		0.05
Sulphur		0.03
COKE.		
Fixed carbon		77.18
Volatile and combustible matter		2.28
Ash		19.93
Moisture		0.60
SiO ₂		6.84
CaO		0.93
Phosphorus		0.09
Sulphur		1.02

¹ *Western Chemist and Metallurgist*, vol. vi. (1910), pp. 269, 323, 347.

LIME.							Per Cent.
CaO	94.34
MgO	trace
SiO ₂	0.37
Al ₂ O ₃ and Fe ₂ O ₃	0.82
Phosphorus	0.08

CHARGE.							Grammes.
Ore	1054
Lime	143
Coke	227

In all the experiments the raw materials were crushed to about a quarter-inch size and the under size retained. The charge was not briquetted in any of the runs, but the ingredients were thoroughly mixed before charging.

TABLE XI.—*Production of Steel directly from Ore-products.*

	I.	II.	III.	IV.	Average.
Carbon per cent.	1.51	1.02	0.99	0.88	...
Silicon „	1.55	0.09	0.25	0.10	...
Phosphorus „	0.16	0.17	0.14	0.05	...
Sulphur „	0.48	0.23	0.32	0.29	...
Kilowatts	3.44	3.35	3.18	3.16	...
Electrode consumption per ton	60.8 kg.
Metal tapped, grammes	205	1052	696	612	...
Extraction per cent.	29.2	94.1	99.1	87.6	...
Kilowatt-hours per kilogramme	24.4	6.9	6.9	7.7	12.8
Kilowatt-years per ton	2.14	0.61	0.61	0.68	1.12

In Experiment No. II., 400 grammes of metal were charged in starting the furnace.

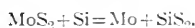
The aim in these experiments was to produce a steel containing 1 per cent. carbon and of low percentage phosphorus and sulphur. No difficulty was experienced in regulating the carbon, but the products were as a rule high in phosphorus and sulphur. This was probably caused by the slag being so basic as not to be fluid enough for intimate contact with the metal. The high sulphur content is derived mostly from the coke, for the ore was of a very high grade. The power consumption and the electrode consumption were high. This was caused by the small scale of the operations and by the

small proportion of metal tapped, because of freezing in the bottom of the furnace.

THE PRODUCTION OF ALLOY STEELS DIRECTLY FROM ORES IN THE ELECTRIC FURNACE.

The production of high-grade alloy steels directly from ores in the electric furnace has been attempted on a small laboratory scale, but has not gone beyond this stage. This is due to the difficulty encountered in producing a steel as free from impurities as is necessary for a very high-grade steel, such as a tool steel or other special steels. Also, working with an ore or concentrate of high value, it is difficult to regulate the carbon content of the product, without losing large amounts of the alloying metal in the slag. Unless the reduced metal is subjected to prolonged heating in the furnace, there is a tendency for a non-homogeneous ingot to be produced because of the gases from the reduction process.

Investigations of Dittus and Bowman on the Direct Production of Molybdenum Steel in the Electric Furnace.—A research was performed by Dittus¹ and Bowman on the production of molybdenum steel directly from iron ore and molybdenite in a small electric furnace holding about 4 kilogrammes of charge and of 5-kilowatt capacity. While the work was qualitative rather than quantitative, as no slag analyses were made, some very interesting results were obtained. The elimination of sulphur from the metal was attempted according to the reaction—



Ferro-silicon was used to accomplish this reaction. In all the experiments the proper amount of ferro-silicon and molybdenite, ground to 0.85 millimetre, and intimately mixed, was enclosed in a small paper tube and added to the bath just before reduction was completed. The iron ore, coke, and lime were crushed to 3 millimetres, and the under size was retained.

¹ *Transactions of the American Electrochemical Society*, vol. xx. (1911), p. 355.

TABLE XII.—*Direct Production of Molybdenum Steel.*

ORE.						Per Cent.
Fe ₂ O ₃	94.50
Al ₂ O ₃	1.52
SiO ₂	4.12
Phosphorus	0.04
Sulphur	0.04

COKE.						
Fixed carbon	77.70
Volatile and combustible matter	2.80
Ash	18.66
FeO	1.23
Al ₂ O ₃	1.41
CaO	1.30
SiO ₂	6.59
Sulphur	0.47
Moisture	0.84

LIME.						
CaO	92.76
MgO	trace
Fe ₂ O ₃ and Al ₂ O ₃	1.90
Phosphorus	0.06
SiO ₂	1.34

FERRO-SILICON.						
Iron	49.70
Silicon	50.0
Sulphur	0.005
Carbon	0.20

TABLE XIII.—*Direct Production of Molybdenum Steel Products.*

	V.	VI.	VII.	VIII.	IX.
Charge:—					
Hæmatite, grammes	3025	756	1512	1512	756
Coke, grammes	660	163	326	326	163
Lime, grammes	412	103	206	206	103
Calculated percentage of molybdenum .	2.50	2.00	...	5.00	0.60
Product:—					
Molybdenum per cent.	1.15	0.45	1.95	2.15	0.45
Carbon per cent.	0.62	1.14	0.71	0.92	0.54
Silicon per cent.	0.91	1.23	2.14	1.10	1.65
Phosphorus per cent.	0.08	0.03	0.04	0.043	0.07
Sulphur per cent.	0.37	0.03	0.025	0.036	0.05
Kilowatts	5	7.5	7.5	7.5	7.5
Metal tapped, grammes	1700	450
Percentage extraction	85.0	90.0
Kilowatt-hours per kilogramme . . .	4.42	16.68
Kilowatt-years per ton	0.50	1.91

These results show qualitatively the possibility of the elimination of sulphur by means of ferro-silicon in making molybdenum steel from molybdenite and iron ore. The steels average 54·5 per cent. lower in molybdenum than calculated. As no slag analyses were made, it is impossible to tell whether the molybdenum was slagged off, volatilised, or the percentage of iron in this steel increased by iron melted out of the bottom of the furnace, or introduced in some other way. The percentage of silicon in the metal was very high. The iron ore was very pure, so that no conclusions can be drawn concerning the elimination of phosphorus.

Previous Research of the Author on the Production of Tungsten Steel directly from Ore in the Electric Furnace.—At the time the author's¹ experiments were made on the production of steel directly from ore, some experiments were conducted upon the production of tungsten steel directly from hæmatite and ferberite concentrates. The iron ore, coke, and lime were the same as used in the production of steel. The ferberite concentrates were of the following percentage composition: 58·72 per cent. WO_3 , 31·08 per cent. FeO , 2·55 per cent. MnO , 4·86 per cent. SiO_2 , 3·46 per cent. CaO , 0·34 per cent. phosphorus, and 0·20 per cent. sulphur. The raw materials were thoroughly mixed in the proper proportions before charging.

TABLE XIV.—*Direct Production of Tungsten Steel.*

	V.	VI.	VII.	VIII.	IX.	X.	XI.
Charge:—							
Hæmatite, grammes	1790	1790	1790	895	1591	1591	1760
Ferberite, „	300	300	300	150	900	900	300
Lime, grammes	214	214	190	95	170	170	160
Coke, „	454	454	470	210	475	475	491
Calculated percentage of tungsten .	10·0	10·0	10·0	10·0	28·5	28·5	10·0
Product:—							
Tungsten per cent.	6·60	10·46	8·95	8·70	15·01	19·01	9·20
Carbon „	3·42	2·42	3·01	2·95	3·56	2·22	2·39
Manganese „	0·32	0·37	0·69	0·46	0·80	0·86	0·69
Silicon „	0·47	0·84	0·72	0·86	0·87	1·02	0·79
Phosphorus „	0·21	0·54	0·03	0·08	0·04	0·08	0·25
Sulphur „	0·28	0·64	0·68	0·64	0·76	0·78	0·66
Kilowatts	5·30	5·30	4·32	61·1	5·68	5·10	5·70
Electrode consumption, kilogs. .	55·2	55·2	40·4	61·1	102·5
Per ton metal tapped, grammes .	1120	760	993	264	510	740	550
Kilowatt-hours per kilogramme .	7·7	9·0	5·6	7·0	10·4	10·4	7·9
Kilowatt-years per ton	0·68	0·79	0·49	0·62	0·91	0·91	0·69

¹ *Western Chemist and Metallurgist*, vol. lxvi. (1910), pp. 269, 323, 347.

The percentage carbon of all the products was high. The double carbide of iron and tungsten could be detected under the microscope. In the experiments on the production of a 10 per cent. tungsten steel, the steels averaged 10·4 per cent. lower in tungsten than calculated. When a 28·5 per cent. tungsten content was sought the loss was 41·7 per cent. This high loss was probably due to hanging of the charge on the walls of the crucible. The greater part of the manganese was either slagged off or volatilised. With the increased acidity of the slag the percentage of silicon in the metal increased. In Experiments Nos. 5 and 6 the slag was so basic as not to be fluid. In all the remaining runs the slag was more fluid, and very little of the phosphorus was concentrated in the metal. At the time of performing the experiments the failure to slag off the sulphur was attributed to the fact that, as the carbon was present in an amount only sufficient to reduce the ore, the operating conditions were not reducing enough to force the sulphur into the slag as calcium sulphide. Also the atmosphere was not oxidising enough to slag off the sulphur as the sulphate. However, subsequent experiments have shown that the failure to eliminate sulphur in this case was due to operating the furnace at too low a temperature. The metal cast was, as a rule, free from large blowholes.

THE PRODUCTION OF FERRO-ALLOYS DIRECTLY FROM ORE IN THE ELECTRIC FURNACE.

Ferro-alloys are manufactured directly from ores by several methods: first, by reduction of the ore with carbon in a blast-furnace or a crucible; second, by the Goldschmidt thermit process; and third, by the direct reduction of the ore with some reducing agent in the electric furnace. The resulting product should be as low in carbon as possible, and free from impurities such as sulphur and phosphorus.

The production of ferro-alloys in the blast-furnace is attended by three difficulties; first, the temperature is too low for the reduction of some of the oxides of the alloying metal, so that only alloys of low melting point can be made; second, it is

difficult to obtain an alloy containing a high percentage of the special metal; and third, it is impossible to produce an alloy low in carbon because of the great excess of carbon in the charge.

The crucible is sometimes used for the production of the more costly alloys directly from ores. It is difficult to obtain a high percentage alloy, and if a graphite crucible is used, the percentage of carbon tends to be high in the metal.

High grade ferro-alloys are now manufactured in large quantities by the Goldschmidt thermit process, in which aluminium is the reducing agent, so that an alloy free from carbon can be made. The manufacturing cost by this method is rather high because of the high cost of aluminium powder, but a more pure product is obtained.

The manufacture of ferro-alloys in the electric furnace consists briefly of the reduction of the ore with carbon, followed by a subsequent decarburisation by the addition of excess of the oxide being reduced. The electric furnace method has several advantages: first, the high temperature possible permits the reduction of the most refractory oxides; second, practically as high a percentage alloy as desired can be made; third, the high temperature permits the use of very basic slags for the removal of impurities; and fourth, decarburisation of the alloy is not difficult. Electric furnace methods have been proposed and used to some extent in which reducing agents other than carbon are employed. Aluminium and silicon have been the most common metals used. The cost of such a process is high, and their use has not become very common.

Ferro-chromium.

Ferro-chromium may be manufactured from chromite in either the crucible, blast-furnace, or electric furnace. In the crucible the chrome ore is reduced with carbon and a flux of lime, borax, fluoride or water-glass. Chrome ore is reduced with some difficulty in the blast-furnace with a fuel consumption of about 3 tons to 1 ton of ferro-chromium produced. Theoretically it should be possible to get a ferro-chromium containing 65 per cent. chromium from an ore con-

taining 60 per cent. Cr_2O_3 and 20 per cent. FeO , but generally a ferro-chromium containing from 30 to 40 per cent. chromium and 6 to 12 per cent. carbon is the product in blast-furnace smelting. In the electric furnace an alloy is made which contains from 60 to 65 per cent. chromium and 5 to 9 per cent. carbon. This first product is subsequently refined and decarburised¹ to give the low carbon alloy. In the refining process, after the accumulated slag has been tapped off, the molten alloy is treated with a mixture of chrome ore and lime. The electrodes are kept away from the metal as much as possible. The decarburising process requires a prolonged superheating which varies with the carbon content desired. At Kanawha Falls,² Virginia, ferro-chromium is produced from chromite in a crucible electric furnace with a power expenditure of 7.9 kilowatt-hours per kilogramme of product. Rossi,³ using aluminium in the electric furnace, has produced ferro-chromium containing 68.24 per cent. chromium, 1.85 per cent. silicon, 1.0 per cent. carbon, 0.5 per cent. aluminium from chromite containing 50.29 per cent. Cr_2O_3 , 16.01 per cent. FeO , 10.72 Al_2O_3 , 4.62 SiO_2 , 16.61 per cent. MgO , 0.01 per cent. sulphur, 1.15 CaO .

TABLE XV.—*Analyses of Typical Ferro-chromium.*

	Crucible.	Blast-Furnace. ⁴	Electric Furnace. ⁵				
			Carbon per Cent. 8-10.	Carbon per Cent. 7-8.	Carbon per Cent. 5-6.	Carbon per Cent. 3-4.	Carbon per Cent. 1.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Chromium . . .	19.8	41.39	64.5	63.5	64.0	64.0	63.5
Iron	22.0	21.5	28.5	31.0	35.0
Carbon . . .	3.8	7.12	9.5	7.5	5.5	3.5	0.60
Silicon	0.21	2.25	5.80	0.4	0.3	0.2
Aluminium	0.80	0.80	0.50	0.40	0.10
Manganese . . .	0.33	1.84	0.15	0.15	0.15	0.15	0.10
Calcium	0.25	0.25	0.25	0.30	0.35
Sulphur	0.04	0.04	0.04	0.04	0.03
Phosphorus	0.052	0.03	0.03	0.03	0.02	0.02

¹ *Transactions of the American Electrochemical Society*, vol. xv. (1909), p. 225.² *Electrochemical Industry*, Nov. 1904, p. 450.³ *Mineral Industry*, 1903, p. 693.⁴ *Foundry Trade Journal*, 1907, p. 424.⁵ *Transactions of the Faraday Society*, vol. vi. (1911), p. 172.

Investigations of Neumann on the Direct Production of Ferro-chromium.—Neumann¹ investigated the use of ferro-silicon as a reducing agent for chromite in the electric furnace in an effort to produce a carbon free alloy. The experiments were performed in an electric furnace holding about 1 kilogramme of charge, and operating with 100 amperes and 30 to 50 volts. Ferro-silicon containing 91·65 per cent. silicon and 1·03 per cent. carbon was used as a reducing agent. The chromite contained 31 per cent. chromium and 13 per cent. iron. A mixture of (150 Al_2O_3 + 100 CaO or 100 Al_2O_3 + 100 CaO) was placed in the furnace, 250 grammes being used. When this was fluid, 700 grammes of a mixture of chrome ore and ferro-silicon were added. About 140 grammes of metal were obtained which contained 38·05 per cent. chromium, 3·09 per cent. silicon, and 1·56 per cent. carbon. In another experiment the metal contained 43·16 per cent. chromium, 2·53 per cent. silicon, and 0·87 per cent. carbon. There seems to have been a heavy loss by slagging of chromium. From these experiments it is evident that the resulting alloy from reduction with silicon will be high in silicon and also contain considerable carbon if there is any present in the silicon used.

Experiments of Moissan.—Moissan² reduced chromite, with carbon as a reducing agent, in the electric furnace, and obtained a ferro-chromium which contained 60·9 per cent. chromium, 31·6 per cent. iron, 6·1 per cent. carbon, and 1·1 per cent. silicon. He also conducted experiments on decarburisation of ferro-chromium. A ferro-chromium containing 61·81 per cent. chromium, 30·02 per cent. iron, 7·53 per cent. carbon, and 0·33 per cent. slag was broken into pieces and fused under a bath of liquid lime. A fine grained metal was obtained which contained 4·2 per cent. carbon. The operation was repeated, and a metal obtained containing 64·0 per cent. chromium, 35·12 per cent. iron, 0·70 per cent. carbon, and 0·22 per cent. slag.

¹ *Stahl und Eisen*, 1908, p. 356.

² "The Electric Furnace" p. 152.

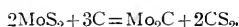
Ferro-molybdenum.

Ferro-molybdenum is generally manufactured in the electric furnace from raw sulphide ores of molybdenum. The composition of some typical molybdenums is given in the following table:—

TABLE XVI.—*Analysis of Ferro-molybdenum.*

	80-85 per Cent. Grade.	Refined 80-85 per Cent. Grade.	Refined 50 per Cent. Grade.
	Per Cent.	Per Cent.	Per Cent.
Molybdenum	85·80	85·200	50·311
Iron	10·963	14·047	48·920
Carbon	3·070	0·450	0·350
Silicon	0·110	0·252	0·300
Sulphur	0·050	0·031	0·030
Phosphorus	0·007	0·020	0·020

Experiments of Guichard.—Guichard¹ obtained crude molybdenum from natural molybdenite by reduction with carbon in the electric furnace. The composition of the metal was 91·80 per cent. molybdenum, 2·10 per cent. iron, and 6·64 per cent. carbon. The operation was performed according to the following reaction:—



The difficulty in the process is to obtain pure metal from impure ores, because there is a tendency for any impurities to concentrate in the metal.

Experiments of Lechner.—Lehner² conducted a series of experiments on the production of a ferro-molybdenum free from sulphur. After several unsuccessful experiments, in which the oxide of other metals were used to decompose molybdenite, and other experiments in which the reducing agent was aluminium, he tried to accomplish the reduction in the electric furnace with a very basic slag according to the following reaction:—

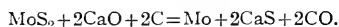
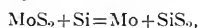
¹ *Comptes Rendus*, vol. cxxii. p. 1270.² *Metallurgie*, vol. iii. (1906), p. 549.

TABLE XVII.—*Experiments of Lehner.*

	I.	II.	III.	IV.	V.
Charge :—					
MoS ₂ , grammes . . .	1500	1500	560	2500	2500
Fe ₂ O ₃ , „	960	2150	2150
CaO, „ . . .	1050	1400	390	4160(CaCO ₃)	4160(CaCO ₃)
Coke, „ . . .	250	385	360	999	999
Product :—					
Molybdenum, per cent. .	90·7	88·3	43·30	50·33	48·72
Iron, „ . . .	2·9	2·89	49·8	45·95	46·56
Carbon, „ . . .	4·10	5·60	6·27	1·70	1·06
Silicon, „	2·95	0·31	1·51	2·61
Sulphur, „ . . .	0·86	0·04	0·05	0·10	0·13

These results show the possibilities of sulphur elimination by means of lime in the electric furnace, but do not show where the molybdenum losses occur, whether in the slag or by volatilisation. An extraction of 85 per cent. was made in Experiment No. 2.

Experiments of Neumann.—Neumann¹ attempted reduction of molybdenite according to the reaction



but obtained poor results. The metal produced contained 2·87 per cent. iron, 2·06 per cent. silicon, 13·89 per cent. sulphur, the remainder being molybdenum.

Ferro-tungsten.

Ferro-tungsten can be manufactured from ores in three ways: first, by direct reduction with carbon in a crucible; second, by reduction in an electric furnace by some reducing agent other than carbon; and third, by direct reduction with carbon in an electric furnace.

In manufacture by the crucible² process concentrates are placed in a clay-lined crucible with the proper proportions of reducing agent and flux, and heated to a high temperature in a gas-fired furnace. There is considerable wear on the crucible in this method. For a 30 per cent. tungsten alloy the crucible will last about three heats, but for a 65 to 75 per cent. alloy

¹ *Stahl und Eisen*, vol. xxviii. (1908), p. 356.

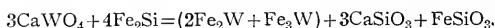
² *Engineering and Mining Journal*, Nov. 12, 1910, p. 959.

they last but one heat. Higher percentage tungsten alloys than this are not made in the crucible furnace.

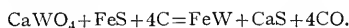
Rossi¹ used a furnace of the old Siemens type, consisting of graphite blocks with a central cavity serving as a cathode, and a vertical movable carbon as the anode. The furnace is charged with scrap aluminium in sufficient quantity to reduce the iron and tungsten oxide to the metallic state. The current melts the aluminium, and then the oxides are introduced.

The iron oxide is first reduced to iron, which forms a bath in which the tungsten dissolves. The aluminium forms a slag on top of the bath. A low carbon alloy can be made. From concentrates containing 69.80 per cent. WO_3 , 5.04 per cent. Si_2O , 20.25 per cent. FeO , he obtains alloys of approximately the following compositions:—75.9 per cent. tungsten, 21.4 per cent. iron, 1.6 per cent. silicon, 0.08 per cent. sulphur, and 0.90 per cent. carbon.

Gin has produced ferro-tungsten by the reduction of scheelite with a bath of 20 per cent. ferro-silicon in the electric furnace, according to the following reaction:—

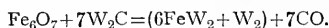


The most common method for the production of ferro-tungsten is by the reduction of wolframite or scheelite concentrates in the electric furnace with carbon as reducing agent, followed by a subsequent decarburisation and refining. Wolframite is readily reduced in this manner, but there is difficulty in the reduction of scheelite. Scheelite² is now smelted by one company with sulphide of iron and carbon in the electric furnace. Lime is also added to flux the silica. The following reaction takes place:—



The product is a ferro-tungsten containing but little carbon.

Decarburisation of Ferro-tungsten.—Ferro-tungsten may be decarburised³ by covering the fused metal in the electric furnace with hammer scale, when the following reaction takes place:—



¹ *Mineral Industry*, 1903, p. 693.

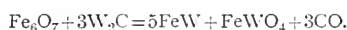
² *Engineering and Mining Journal*, vol. xciii. (1912), p. 173.

³ *Transactions of the American Electrochemical Society*, vol. xiii. (1908), p. 481.

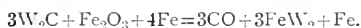
TABLE XVIII.—*Typical Ferro-tungsten.*¹

	I.	II.	III.
	Per Cent.	Per Cent.	Per Cent.
Tungsten	73.0	78.5	83.0
Carbon	3.5	1.7	0.600
Iron	19.0	18.5	15.500
Silicon	0.400	0.3	0.400
Manganese	3.5	0.4	0.200
Calcium	trace	0.1	0.151
Arsenic	0.400	0.1	0.100
Tin	0.100	0.05	0.050
Sulphur	0.050	0.04	0.040
Phosphorus	0.030	0.015	0.015

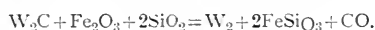
The reaction is not quantitative, since there is always formed some ferrous tungstate:—



By this reaction it is possible to make ferro-tungsten containing 80 per cent. tungsten and less than 0.5 per cent. carbon. Reduction of carbon cannot be made lower than 0.3 per cent. carbon by this method. Ferro-tungsten with less than 80 per cent. tungsten may be made by adding metallic iron to the bath and decarburising with oxide of iron and hammer scale:—



This method will yield alloys with as low as 0.15 per cent. carbon. Decarburising with iron oxide has a tendency to cause a loss of tungsten in the slag by the formation of tungstate of iron. This may be reduced somewhat by making the decarburising slag rather acid when ferrous silicate is formed:—



Experiments of Stassano.—Stassano² conducted experiments in 1908 on the manufacture of ferro-tungsten directly from wolframite concentrates in a 75-kilowatt electric furnace, using charcoal as a reducing agent. The concentrates, charcoal, and lime were crushed and briquetted with a 25 per cent. solution of sodium silicate as a binder.

¹ *Transactions of the Faraday Society*, vol. vi. (1911), p. 172.

² *Electrochemical and Metallurgical Industry* (1908), p. 315.

TABLE XIX.—*Experiments of Stassano.*

Ore.	Charge, Parts.		I.	II.	III.	Average.
WO ₃ per cent. 69·80	Wolframite 1000	W . . .	58·00	65·66	69·70	...
SiO ₂ " 2·00	Charcoal . 190	C . . .	2·40	2·062	2·508	...
FeO " 20·50	Lime . . 40	Mn . . .	3·192	3·50	3·60	...
MnO " 7·30	Na ₂ SiO ₃ . 80	Si . . .	1·244	1·02	1·30	...
S " 0·20	...	P . . .	trace	trace	trace	...
P " trace	...	S . . .	trace	trace	trace	...
Kilowatt-hours per kilogramme	6·0	6·5	7·5	6·6
Kilowatt-years per ton	0·69	0·74	0·86	0·76

Theoretically the ferro-tungsten should have contained 71·5 per cent. tungsten, 20·6 per cent. iron, 7·1 per cent. manganese, and 1·0 per cent. silicon. These experiments showed a possibility of reduction of wolframite with carbon in the electric furnace, but do not show where the loss in tungsten occurred. It is not apparent whether the lower tungsten content than the theoretical was the result of slag losses or the presence of some iron in the furnace, not mentioned here, which diluted the alloy.

PART II.

RESEARCH UPON THE PRODUCTION OF STEELS AND FERRO-ALLOYS DIRECTLY FROM ORES IN THE ELECTRIC FURNACE.

Experimental Furnaces.

In previous researches with small electric furnaces having a conducting hearth difficulty had been experienced because of the formation of accretions on the walls above the smelting zone. It was also observed that the larger the electrode the less difficulty there was in keeping the furnace charge hot. This was probably due to a more even distribution of the current throughout the molten charge. If a round or square electrode in a circular or a square crucible was made excessively large in cross section, much beyond the amount theoretically necessary, there would be so great a loss of heat by conducting through the electrode, and so much difficulty in

charging, that the advantage gained by more even distribution of the current would be more than off-set. In an endeavour to gain the conditions desired, a thin flat electrode of rectangular cross section was used in a crucible of rectangular cross section.

In the course of the experiments performed, furnaces of three different sizes were used, all of the same general type. The first furnace was designed for three-phase alternating current, but after much of it had been constructed it was found that three-phase power could not be obtained. As the type of furnace was such that single-phase alternating current could be employed, it was finished as originally designed. This furnace is shown in Fig. 1, and was used only in the preliminary experiments. The original three-phase furnace had been designed for 20 kilowatts capacity, and that amount of single-phase current was expected, but the generator did not deliver on an average more than 8 kilowatts at the furnace. As a result, after the preliminary experiments the crucible of the first furnace was reduced to one half of its original size.

The first furnace, Fig. 1, consisted of a rectangular crucible lined with magnesite brick, with the current passing into the crucible through two upper graphite electrodes, through the charge, and then through the bottom of the furnace, which was made of iron rods imbedded in dead burned magnesite. This crucible was surrounded by firebrick, and roofed with fireclay tiles. Iron bands held the bricks together, and could be adjusted to allow for expansion. The upper electrodes passed between tiles, and were surrounded by asbestos to prevent heat losses and leakage of gases. A rectangular opening was left between the tiles around the electrodes for introduction of the charge. There was one tap-hole at the bottom of the crucible and in the middle of one side. The crucible was $11\frac{1}{2}$ inches by 1 foot $3\frac{1}{2}$ inches cross section at the top, and 6 inches by 1 foot 2 inches at the bottom, with a depth of 1 foot. The total volume of the crucible was 1600 cubic inches. Above the crucible there was a space 1 foot 3 inches long, 4 inches wide, and $4\frac{1}{2}$ inches deep. The exterior dimensions of the furnace were, width 3 feet $3\frac{1}{2}$ inches, length 4 feet 6 inches, and height 3 feet 1 inch.

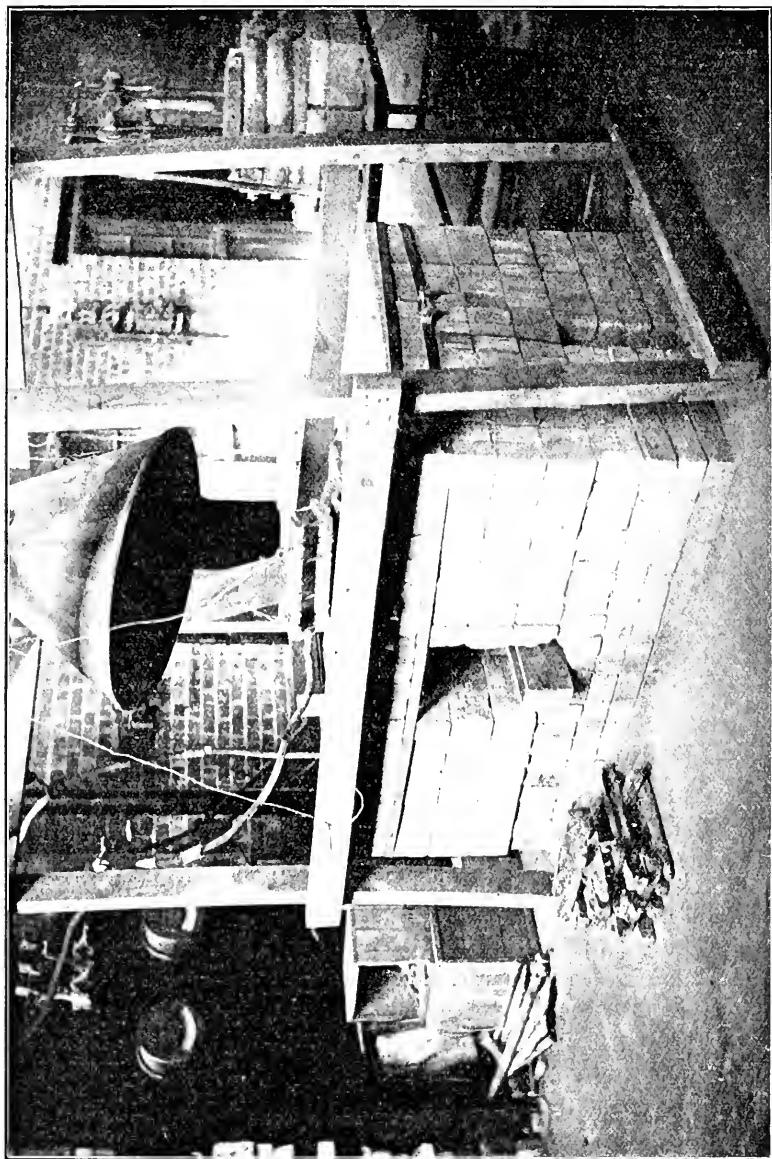


FIG. 1.—Experimental Furnace.

Each of the two graphite electrodes consisted of two Acheson graphite plates, $\frac{1}{2}$ inch by 6 inches by 24 inches, which were fastened side by side so as to give an electrode $\frac{1}{2}$ inch by 12 inches in cross sections. The total electrode cross section was thus 12 square inches, or the equivalent of one round electrode $3\frac{1}{8}$ inches in diameter. The contact with each electrode was made by two copper plates, 14 inches by 4 inches by $\frac{1}{4}$ inch, placed on each side of the graphite plates, and held in place in a cast iron frame running the width of the electrodes. The lug on the cable to the switchboard was bolted to the copper plates. The current was conducted close to the furnace by one cable, but was subdivided at the furnace into two cables, one leading to each of the upper electrodes. The copper plates were held against the graphite plates by set screws. Each electrode was suspended by wire running over a pulley on a wooden framework around the furnace. By careful adjustment of weights on the wires, close and easy adjustment of the electrodes was made possible. The whole bottom of the furnace acted as the other electrode. It consisted of a soft iron plate $\frac{1}{2}$ inch thick, 6 inches wide, and 1 foot 2 inches long, into which were screwed 24 circular soft iron rods of $\frac{1}{2}$ -inch diameter at intervals of from $1\frac{1}{4}$ inches to 2 inches. This was filled in with magnesite mixed with a solution of water glass. The bottom connection was made by bolting the lug of the cable from the instrument board to the iron plate. A space $4\frac{1}{2}$ inches wide by $7\frac{1}{2}$ inches deep, running the length of the furnace, was left beneath the crucible to permit the passage of air for cooling the iron plate if necessary. Owing to the short duration of experiments, it was not considered necessary to water-cool the electrodes.

The lining of the crucible was of magnesite brick with a thin internal lining of two parts of dead burned magnesite mixed with one part of magnesite cement, and enough water glass to make the mixture pasty. This lining was from 4 to 6 inches thick, and extended to the top of the crucible. The hole in the roof was lined with fireclay tile, as the basic slags were not to come in contact with it to great extent.

The second furnace was of similar design to the first, but the crucible was reduced to about half the original length and

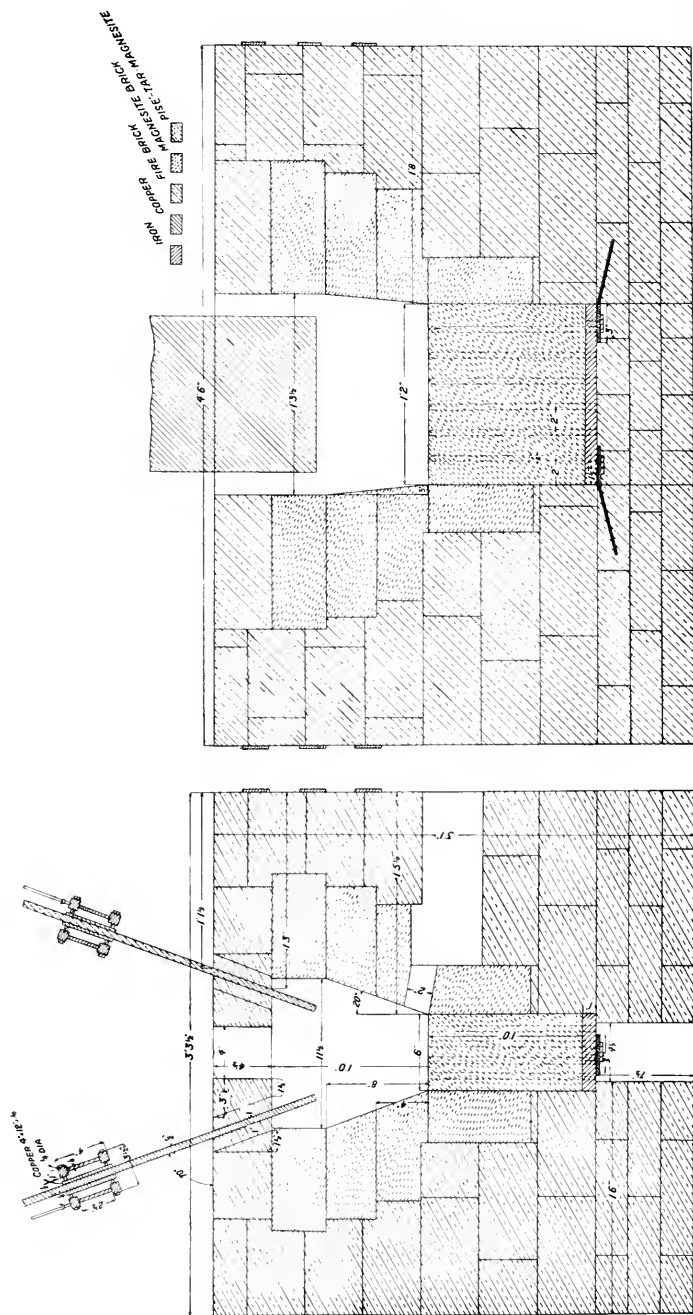


FIG. 2.—Experimental Smelting Furnace.

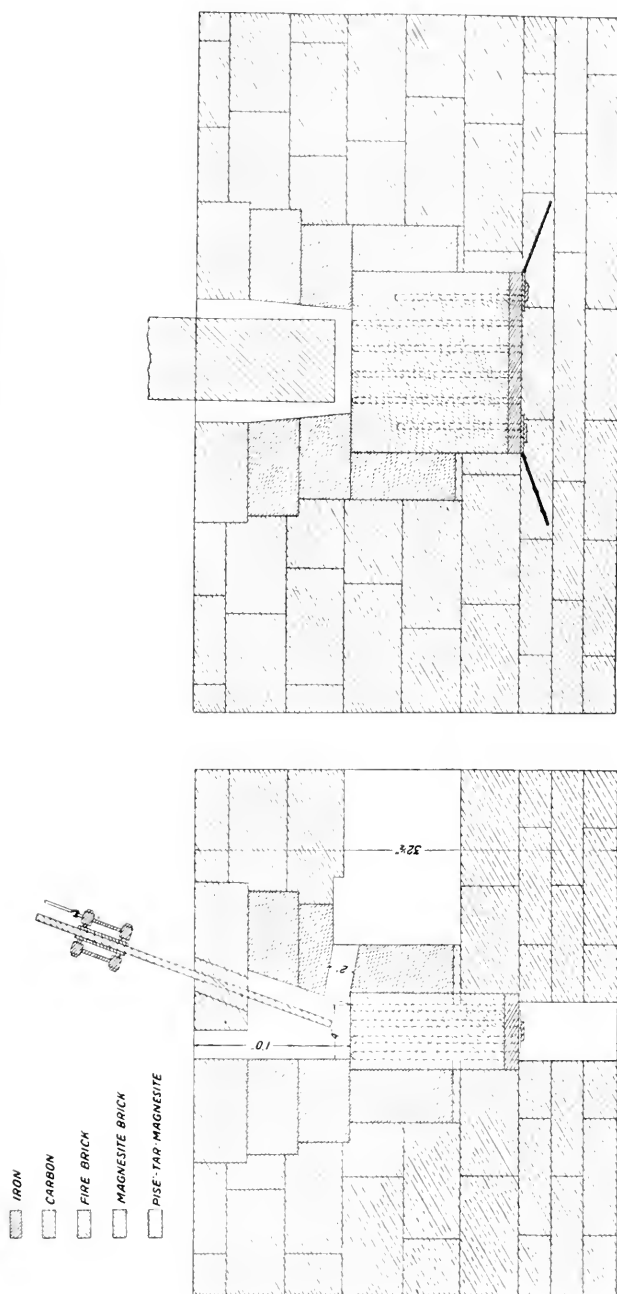


FIG. 3.—Experimental Smelting Furnace.

three-quarters of the width, being 9 inches long, 4 inches wide at the bottom, and 12 inches deep, with a total interior volume of about 700 cubic inches. Each of the upper electrodes consisted of one graphite plate $\frac{1}{2}$ inch by 6 inches by 24 inches. The charging opening was left in the centre of the furnace as before. This furnace was used in experiments on steel directly from ore and on the production of ferro-tungsten. It operated with 10 to 12 kilowatts, but as the power was very low at times it was necessary to reduce the size still further.

The third furnace, Fig. 2 and Fig. 3, had one upper flat graphite electrode $\frac{1}{2}$ inch by 6 inches by 24 inches, and the conducting hearth as in the previous furnaces. The electrode was inclined so that the bottom was about in the centre of the crucible. It was held in place as before with a fireclay tile, which covered the entire top of the crucible except a space 2 inches wide at the side, through which the charging was done. Another fireclay tile was placed over the opening. The interior dimensions of the crucible were 4 inches wide, 8 inches long, and 8 inches deep, with a total volume of 254 cubic inches.

Apparatus and Instruments.

Electrical energy was supplied by a single-phase alternating current generator, manufactured by the General Electric Company. This machine was rated at 1040 volts no load, 1155 volts full load. It was used ordinarily on a lighting circuit with a frequency of 125 cycles, which is much too high a frequency for efficient electric furnace operation. The generator was rated at 30 kilowatts capacity, but as it was necessary to operate it with a series coil short circuited across the brushes, not more than from 6 to 12 kilowatts were delivered at the furnace. This arrangement protected the machine from any overload or a short circuit, which would cause the voltage to drop due to armature reaction and reactance.

The voltage from the generator was stepped down by six General Electric Company transformers of rated capacity of 16 kilowatts, but which could be overloaded to about 20 kilowatts without excessive heating. Number 0000 rubber

insulated cable of 300 amperes capacity connected the transformers with the instrument board.

On the instrument board a circuit breaker was used to close the circuit, but it was set at such a high amperage that it would not break with excessive current. It was found more convenient to place fuses on the primary side of the circuit for this purpose. The amperage was read from two Westinghouse Electric Company ammeters, each of 300 amperes capacity, and connected in parallel with each other, but in

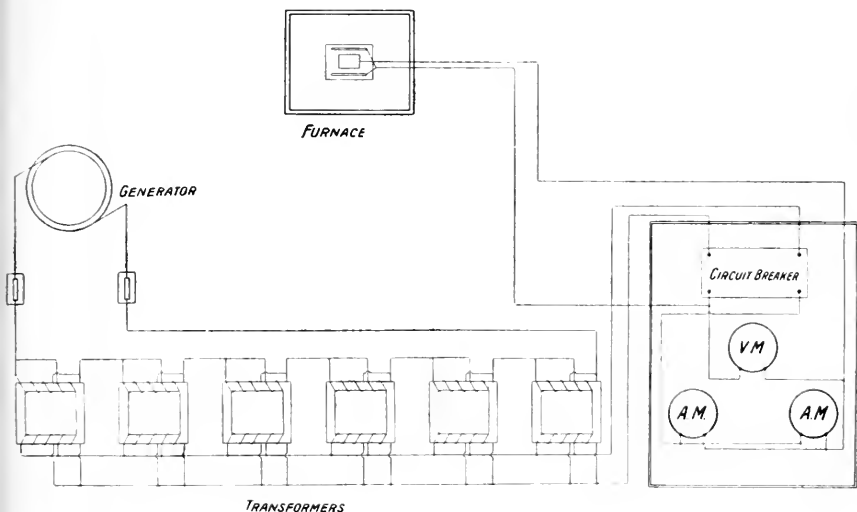


FIG. 4.—Diagram of Furnace Connections.

series with the line. The voltage was determined with a portable Weston voltmeter of 75 volts range. No wattmeter was used. A power factor of 0.80 has been assumed in calculating the actual power on the furnace.

All tappings were made into a cast iron mould, 15 inches long, $4\frac{1}{2}$ inches deep, and $1\frac{1}{2}$ to 2 inches wide, internal dimensions. Temperature determinations were not made, because of the difficulty in doing it accurately in such small scale work. The electrical connections are shown in the accompanying diagram, Fig. 4.

THE PRODUCTION OF STEEL DIRECTLY FROM ORE IN THE ELECTRIC FURNACE.

Theoretical Considerations.

In calculating the amounts of carbon and electrical energy theoretically necessary to produce 1 ton of steel directly from ore, the following assumptions are made:—First, the ore is to be hæmatite, containing 60 per cent. iron; second, the iron content of the charge is to be 50 per cent. of the weight of the ore and lime; third, the steel is to contain 99 per cent. iron, 0·5 per cent. carbon, 0·2 per cent. manganese, 0·1 per cent. silicon, phosphorus and sulphur a trace; fourth, the charge is to enter the furnace at a temperature of 0° C., and the ore and lime are to be free from water and carbon dioxide; and fifth, the departing flue gases contain 40 per cent. carbon dioxide, and have a temperature of 200° C. In the calculations the following constants¹ are used:—

In reducing 1 kilogramme Fe from Fe_2O_3 1746 calories are absorbed.							
„	1	„	Si	„	SiO_2	6428	„ „ „
„	1	„	Mn	„	MnO_2	2278	„ „ „
In oxidising 1 „ C to CO 8100 „ „ developed.							
„	1	„	C	„	CO_2	2430	„ „ „

In melting and heating 1 kilogramme of steel 350 calories are required. In melting and superheating 1 kilogramme of slag 600 calories are required. The specific heat of dry furnace gases per kilogramme is 0·245 calory. In expelling CO_2 from 1 kilogramme of CaCO_3 , 430 calories are used.

I. *Consumption of Carbon.*—Formulæ of reactions:—

- (a) $14 \text{ Fe}_2\text{O}_3 + 30 \text{ C} = 12 \text{ CO}_2 + 18 \text{ CO} + 28 \text{ Fe}.$
 (b) $14 \text{ SiO}_2 + 20 \text{ C} = 8 \text{ CO}_2 + 12 \text{ CO} + 14 \text{ Si}.$
 (c) $14 \text{ MnO}_2 + 20 \text{ C} = 8 \text{ CO}_2 + 12 \text{ CO} + 14 \text{ Mn}.$

For the production of 1 ton (1000 kilogrammes) of steel containing 99 per cent. iron, 990 kilogrammes of Fe are required, which are obtained from 1414·28 kilogrammes of Fe_2O_3 (a). For this reduction 227·29 kilogrammes carbon are necessary, and 654·34 kilogrammes of gases ($\text{CO}_2 + \text{CO}$) are formed.

¹ Richard's Metallurgical Calculations.

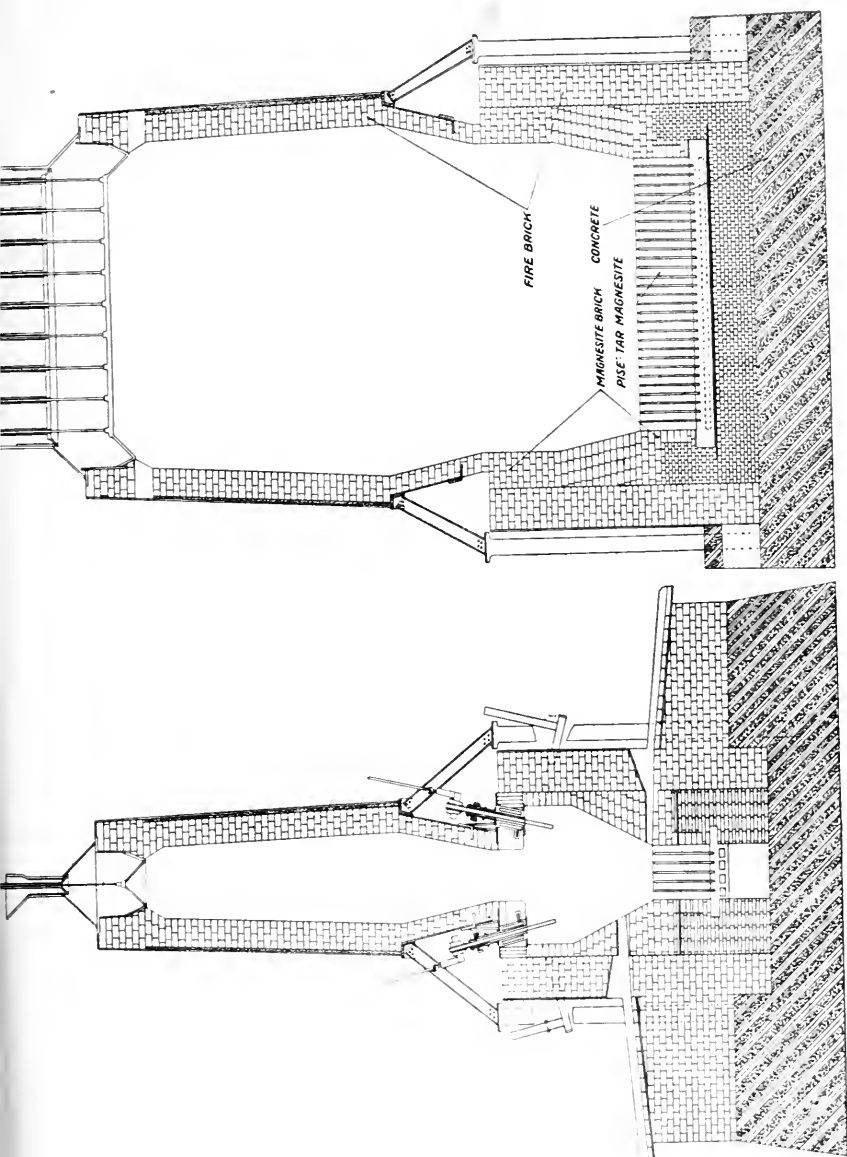


FIG. 5.—Electric Smelting Furnace.

To give 1 ton of steel containing 0.10 per cent. silicon 1 kilogramme silicon is necessary, which is obtained from 2.13 kilogrammes SiO_2 (b). For this reduction 0.61 kilogramme carbon is necessary, and during the reduction 1.75 kilogrammes of gases ($\text{CO}_2 + \text{CO}$) are formed.

For 1 ton of steel containing 0.20 per cent. manganese 2 kilogrammes of manganese are required, which are obtained from 3.16 kilogrammes MnO_2 . For this reduction 0.62 kilogramme carbon is necessary, and during the reduction 1.78 kilogrammes of gases ($\text{CO}_2 + \text{CO}$) are evolved.

Total amount of carbon required:—

	Kilogrammes.
In reduction of 990 kilogrammes iron	227.29
„ „ 1 kilogramme silicon	0.61
„ „ 2 kilogrammes manganese	0.62
In the steel	5.00
Total	<u>233.52</u>

II. *Amount of Slag.*—As the charge, ore and lime, contains 50 per cent. iron, 990 kilogrammes of iron require a charge of 1980 kilogrammes, which corresponds to 1414.28 kilogrammes Fe_2O_3 .

	Kilogrammes.
Slag-making substances	565.72
Amount SiO_2 and MnO_2 deducted	<u>5.29</u>
Total slag per ton of steel	560.43

III. *Amount of Gas Evolved.*—

	Kilogrammes.
In reduction of Fe ($\text{CO}_2 + \text{CO}$)	654.34
„ „ Si ($\text{CO}_2 + \text{CO}$)	1.75
„ „ Mn ($\text{CO}_2 + \text{CO}$)	<u>1.78</u>
Total gas per ton of steel	657.87

IV. *Heat of Combustion of Carbon.*—If 1 kilogramme of carbon combines with oxygen to form a gas mixture which volumetrically contains 40 per cent. CO_2 and 60 per cent. CO , heat is developed as follows:—

	Kilogrammes	Calories.
C to $\text{CO}_2 - 0.4 \times 8100$	3240	
C „ $\text{CO} \quad 0.6 \times 2430$	1458	
Total heat of combustion of carbon	<u>4698</u>	

V. *Heat Balance*.—Amount of heat required :—

	Calories.
To reduce 990 kilogrammes Fe from Fe_2O_3 , 990×1746 .	1,728,540
„ 1 kilogramme Si „ SiO_2 1×6428 .	6,428
„ 2 kilogrammes Mn „ MnO_2 , 2×2278 .	4,556
To melt and superheat 1000 kilogrammes steel, 1000×350 .	350,000
„ „ 560.43 „ slag, 560.43×600 .	336,258
To raise the temperature of 657.87 kilogrammes ($\text{CO}_2 + \text{CO}$) to 200°C ., $200 \times 0.245 \times 657.87$	32,236
Total	2,458,018

Amount of heat supplied :—

	Calories.
By combustion of 233.52 kilogrammes carbon, 233.52×4698 .	1,097,077
Amount of heat furnished by electric current	1,360,941
Total	2,458,018

The theoretical amount of electrical energy is $\frac{1,360,941}{857} = 1588$ kilowatt-hours per ton, which is equivalent to 1.58 kilowatt-hours per kilogramme, 0.181 kilowatt-years per ton, and 5.51 tons per kilowatt-year.

Under the conditions assumed, to produce a ton of steel of the composition stated requires 234 kilogrammes of pure carbon, and 1588 kilowatt-hours per ton, or 1.58 kilowatt-hours per kilogramme, or 0.181 kilowatt-years per ton, which is equivalent to 5.51 tons of steel per kilowatt-year.

VI. *Heat Balance, using Limestone instead of Lime*.—With limestone used in the place of lime the amount of limestone necessary to replace 330 kilogrammes of lime used for the production of 1 ton of steel is 634 kilogrammes. This requires 269,620 calories for the expulsion of carbon dioxide.

With limestone the amount of heat required :—

	Calories.
Previously stated (V.)	2,458,018
To expel CO_2 from 634 kilogrammes limestone, 634×430 .	269,620
Total	2,727,638

Amount of heat supplied :—

	Calories.
Combustion of carbon (V.)	1,097,077
Amount of heat from electric current	1,630,561
Total	2,727,638

The theoretical amount of electrical energy required is $\frac{1,630,561}{857} = 1902$ kilowatt-hours per ton, which is equivalent to 1.90 kilowatt-hours per kilogramme, to 0.217 kilowatt-year per ton, or 4.60 tons per kilowatt-year.

Experiments.

Preliminary Experiments.—To determine the working conditions of the furnace shown in Fig. 1, the furnace was operated for several days in making pig iron. The charge consisted of ore, lime, and coke of a total weight of about 20 kilogrammes. The furnace started readily with a cold charge, but heated up very slowly. After a period of from four to six hours it was hot, but as the length of any experiment was limited by power conditions to six or seven hours, it was decided to reduce the size of the crucible by one half, Fig. 2, and run on smaller charges. When the crucible had once become hot the furnace operated steadily, with little regulation of electrodes necessary. The electrodes wore very evenly. The joining of the two graphite plates to form the electrode did not cause small arcs to set up in the cracks between them, nor any considerable unevenness of wearing. As the result of the preliminary experience, it was evident that the furnace was too large for the amount of power available if rapid experimental work was to be done, and that the flat electrode was going to work satisfactorily.

Calculations.—Because of the impossibility of tapping a small furnace cleanly after each experiment, the percentage of total extraction is sometimes low. For this reason it seemed advisable, in order to more closely represent large-scale working, to calculate the theoretical weight of steel present, and from the loss of iron in the slag calculate the total weight of steel which would have been tapped if it were mechanically possible, considering all iron to be available which did not pass into the slag.

In the first runs the slag was weighed, but as uniform results did not seem possible the slag was calculated from the analyses in each case on the basis that all the lime charged passed into the slag. As in some of the experiments a large

part of the lining passed into the slag, sometimes the weight of the slag appears to be greater than the slag-forming materials actually charge.

The results calculated concerning power consumption are based upon actual consumption at the furnace terminals. The metric ton and the year of 8760 hours are used throughout all the calculations.

TABLE XX.—*Steel. Raw Materials.*

HÆMATITE.							Per Cent.
Fe ₂ O ₃	81.40 (57.0 Fe)
SiO ₂	9.25
Al ₂ O ₃	4.30
CaO	1.00
MgO	0.40
MnO	0.15
Phosphorus	0.124
Sulphur	0.14
COKE.							
Fixed carbon	81.48
Volatile and combustible matter	0.25
Ash	17.92
Moisture	0.35
FeO	1.20
SiO ₂	13.62
CaO	0.85
Phosphorus	0.08
Sulphur	0.54
LIMESTONE.							
CaCO ₃	97.50 (54.5 CaO)
MgO	trace
SiO ₂	0.70
Al ₂ O ₃	0.80
Phosphorus	0.008
FLUORSPAR.							
CaF ₂	90.00
CaCO ₃	0.80
Al ₂ O ₃	8.50
FERRO-SILICON.							
Silicon	50.00
Iron	49.70
Carbon	0.20
Sulphur	0.005

The results of all experiments performed in this research were tabulated according to the form shown in the two following experiments:—

EXPERIMENT No. 1.—*Object: The Production of a Soft Steel.*

Charge:—						Kilogrammes.
Hæmatite	6.82
Coke	1.02
Limestone	3.66

Record of Run.

Time.	hr.	min.	Amperes.	Volts.]	Kilowatts.	Remarks.
8	45		500	5	2.00	Furnace started with coke in the bottom.
8	55		220	50	8.80	Charged.
9	5		180	58	8.34	"
9	15		90	59	4.25	"
9	25		300	52	12.51	"
9	35		320	42	10.80	Charge all added.
9	45		260	59	12.26	
9	55		260	46	9.58	
10	5		340	37	10.69	Charge reduced.
10	15		265	44	9.35	
10	25		360	33	9.50	Tapped 1.22 kilogrammes of steel. Could not tap cleanly. Metal was frozen on bottom of furnace. The slag contained metallic shots. Power was very variable.

Length of run	1 hour 40 minutes.
Mean volts on the furnace	43
" amperes	"	269
" kilowatts	"	8.94
Kilowatt-hours	14.95
Kilogrammes of carbon per kilogramme of iron	0.213
Loss in weight of electrodes	60 grammes.
Electrode consumption per ton of metal tapped	49.4 kilogrammes.
" " "	"	"	"	reduced	.	.	.	18.2 "
Calculated weight of steel	3.89 "
Weight of steel tapped	1.22 "
" slag	5.54 "
Loss of iron in the slag per cent.	15.25 (0.59 kilog.).
Weight of metal reduced	3.30 kilogrammes.
Kilowatt-hours per kilogramme of metal tapped	12.22
" " "	"	"	"	reduced	.	.	.	4.52
Kilowatt-years per ton	"	"	"	tapped	.	.	.	1.40
" " "	"	"	"	reduced	.	.	.	0.51

*Analysis of Metal.**Analysis of Slag.*

	Per Cent.		Per Cent.
Carbon	0.08	SiO ₂	28.40
Manganese	0.17	CaO	37.46
Silicon	0.07	MgO	11.60
Phosphorus	0.088	FeO	14.23
Sulphur	0.027	Al ₂ O ₃	5.52

The carbon content of the charge in this run was made, slightly less than would be required according to formula (a),

to note the effect on the product, which was soft and malleable as cast. Under the microscope, after etching with picric acid, the section showed ferrite and pearlite.

EXPERIMENT No. 2.—*Object: The Production of a Soft Steel.*

Charge:—		Kilogrammes.
Hæmatite	6·82
Coke	1·02
Limestone	4·04

Record of Run.

Time. hrs. min.	Amperes.	Volts.	Kilowatts.	Remarks.
10 28	50	64	2·56	Furnace hot from No. 1 started easily.
10 38	285	43	9·48	Charged.
10 48	185	51	7·55	"
11 8	85	56	3·82	"
11 18	85	59	4·04	"
11 28	330	37	9·80	Charge all added.
11 38	300	39	9·35	
11 48	305	40	9·78	
11 58	270	43	9·31	Charge all reduced.
12 8	290	40	9·29	Tapped 0·91 kilogramme iron, slag very basic, and contained shots of metal. Difficulty in tapping. Furnace was not tapped cleanly. There was metal frozen on the bottom. Had to tap at a higher level.

Length of run	1 hour 40 minutes.
Mean volts on the furnace	47
" amperes	"	223
" kilowatts	"	8·51
Kilowatt-hours	14·20
Kilowatt per kilogramme	0·213
Loss of weight of electrodes	60 grammes.
Electrode consumption per ton of metal tapped	65·9 kilogrammes.
" " " reduced	18·0 "
Calculated weight of steel	3·89 "
Weight of metal tapped	0·91 "
" slag	5·67 "
Loss of iron in the slag per cent.	14·49 (0·56 kilog.).
Weight of metal reduced	3·33 kilogrammes.
Kilowatt-hours per kilogramme of metal tapped	15·61
" " " reduced	4·26
Kilowatt-years per ton of metal tapped	1·79
" " " reduced	0·49

Analysis of Metal.

	Per Cent.
Carbon	0·16
Manganese	0·08
Silicon	0·04
Phosphorus	0·067
Sulphur	0·045

Analysis of Slag.

	Per Cent.
SiO ₂	22·88
CaO	40·25
MgO	12·61
FeO	12·85
Al ₂ O ₃	5·58

The carbon content of the charge was the same as in Experiment No. 1, but the limestone was increased. This made the slag too basic, and it contained shots of metal. The steel was soft and malleable as cast. A section showed ferrite and pearlite, Fig. 13, Plate XV.

SERIES I. *Several Variables.*—A series of eight experiments were made, in which both the limestone and coke were varied in the charge. A furnace similar to that shown in Fig. 1, but of half of the size was used. Seven of these experiments were successful, the condensed results of which are given in Table XXI. The manner in which the record of each experiment performed in this research was recorded, and the form of deriving calculations is shown, in the detailed record of Experiments No. 1 and No. 2, given below. The condensed tables of the results of the different series of experiments are compiled from similar records.

At the close of Experiment No. 8, Table XXI., the furnace was cleaned out and relined with dead burned ground magnesite, made to a paste with water-glass. Resetting of the magnesite brick was not necessary, but any cavities were filled with magnesite. During the eight experiments about 2 inches of metal had accumulated upon the floor of the furnace. This metal was removed, and weighed 12.95 kilogrammes.

This weight of steel, added to that tapped in each experiment, Table XXI., made the total weight of steel obtained for the eight experiments 26.68 kilogrammes. The calculated weight of the steel, allowing no slag loss, was 31.24 kilogrammes. On this basis the percentage extraction was 85.70 per cent. The total steel reduced in the eight experiments was 28.50 kilogrammes. On this basis 93.90 per cent. of the steel reduced was tapped, and the calculated weight of the steel reduced was 91.20 per cent. of the total calculated weight of the steel. The mass of metal removed from the furnace was malleable.

SERIES II. *Variation of Coke in the Charge.*—Beginning with Experiment No. 9, a series of five experiments was made to determine the effect of varying the amount of coke in the charge, the other components of the charge remaining con-

TABLE XXI.—*The Production of Steel directly from Ore.*

Experiment No.	1.	2.	3.	4.	5.	6.	8.	Total 1 to 8.	9.	10.	11.	12.
Charge: Hematite, kilogrammes	6.82	6.82	6.82	6.82	6.82	6.82	6.82	...	6.82	6.82	6.82	6.82
" Coke, "	1.02	1.02	1.25	1.25	1.25	1.36	1.36	...	1.25	1.31	1.36	1.42
" Limestone, "	3.66	4.04	4.52	3.34	3.66	3.34	2.05	...	2.05	2.05	2.05	2.05
" Fluorspar, "
Product: Steel, C per cent.	0.08	0.16	0.29	0.53	0.33	1.16	1.04	...	0.48	1.06	1.57	1.64
" " Mn "	0.17	0.08	0.18	0.15	0.10	0.10	0.07	...	0.15	1.07	0.13	0.12
" " Si "	0.07	0.04	0.02	0.07	0.04	0.06	0.08	...	0.12	0.13	0.16	0.23
" " P "	0.088	0.067	0.057	0.063	0.082	0.030	0.010	...	0.026	0.041	0.089	0.107
" " S "	0.027	0.045	0.050	0.045	0.020	0.051	0.033	...	0.147	0.085	0.067	0.048
" Slag, SiO ₂ "	28.40	22.88	22.32	22.20	26.36	24.86	33.28	...	31.28	36.73	37.24	41.20
" " CaO "	37.46	40.25	46.20	41.76	45.60	45.40	35.80	...	39.03	36.25	30.20	32.16
" " MgO "	11.60	12.61	5.61	6.60	7.25	7.65	7.98	...	10.90	7.75	11.61	8.89
" " FeO "	14.23	12.85	6.33	8.58	7.59	7.85	7.87	...	8.73	5.26	2.53	0.50
" " Al ₂ O ₃ "	5.52	5.58	17.01	19.07	7.47	10.95	11.81	...	7.12	5.88	12.38	17.45
Kilogramme carbon per kilogramme iron	0.213	0.213	0.263	0.263	0.263	0.286	0.286	...	0.263	0.274	0.286	0.299
Calculated steel, kilogrammes	3.89	3.89	3.90	3.91	3.91	3.93	3.93	...	3.93	3.93	3.97	3.98
Steel tapped, "	1.22	0.91	3.60	1.37	0.91	1.28	2.96	...	0.90	2.05	2.34	3.18
Steel reduced, "	3.30	3.33	3.63	3.61	3.64	3.67	3.66	...	3.71	3.79	3.90	3.96
Per cent. tapped "	31.30	23.30	92.30	35.00	23.20	32.60	80.80	...	22.29	52.10	58.90	80.00
Per cent. reduced "	84.95	85.60	93.10	92.30	93.00	93.40	93.20	...	94.45	96.20	98.30	99.60
Per cent. iron slagged "	15.25	14.49	7.08	7.71	6.88	6.75	6.82	...	5.64	3.60	1.80	0.49
Electrode consumption per ton of steel
tapped, kilogrammes	49.4	65.9	16.82	123.9	186.8	187.5
Electrode consumption per ton of steel
reduced, kilogrammes	18.2	18.0	16.50	47.1	46.7	65.3
Kilowatt-hours per kilogramme tapped .	12.22	15.61	5.60	10.78	15.45	15.21	6.01	...	19.70	8.69	6.69	4.92
" " reduced, "	4.52	4.26	5.55	4.18	3.87	5.29	4.88	...	4.75	4.82	4.03	3.94
" " years per ton tapped "	1.40	1.79	0.64	1.34	1.77	1.74	0.69	...	2.25	0.99	0.76	0.56
" " " reduced "	0.51	0.49	0.63	0.48	0.42	0.61	0.55	...	0.54	0.55	0.46	0.45

1 Including 12.95 kilogrammes cleaned out of the furnace.

TABLE XXI.—*continued.*

Experiment No.	13.	14.	15.	16.	18.	19.	20.	21.	Total 9 to 22.	23.	Total 1 to 23.	Aver- age 1 to 23.
Charge: Haematite, kilogrammes	6·82	6·82	6·82	6·82	6·82	6·82	6·82	6·82	...	13·64
" Coke, "	1·48	1·31	1·31	1·31	1·31	1·31	1·31	1·31	...	2·56
" Limestone, "	2·05	2·27	2·50	2·73	2·66	2·64	2·53	2·47	...	5·45
" Fluorspar, "	0·054	0·086	0·17	0·23	...	0·057
Product: Steel, C per cent.	1·71	1·19	0·92	0·44	0·74	1·44	1·51	2·25	...	0·39
" " Mn "	0·13	0·08	0·07	0·08	0·11	0·10	0·08	0·10	...	0·08
" " Si "	0·24	0·11	0·11	0·14	0·16	0·12	0·07	0·06	...	0·12
" " P "	0·121	0·039	0·072	0·057	0·055	0·053	0·030	0·070	...	0·031
" " S "	0·044	0·120	0·107	0·063	0·027	0·035	0·049	0·060	...	0·048
" Slag, SiO ₂ "	39·75	34·09	32·72	29·48	29·28	29·44	28·00	27·00	...	30·48
" " CaO "	34·85	37·40	41·90	46·70	44·90	49·60	48·10	50·10	...	31·30
" " MgO "	10·70	9·90	10·50	2·22	3·15	1·03	3·24	3·66	...	13·39
" " FeO "	3·50	7·00	5·83	7·29	8·18	6·12	7·29	7·00	...	15·20
" " Al ₂ O ₃ "	10·50	9·46	7·31	12·17	9·73	10·11	8·97	9·57	...	9·28
Kilogramme carbon per kilogramme iron	0·311	0·274	0·274	0·274	0·274	0·274	0·274	0·274	...	0·268
Calculated steel, kilogrammes.	3·98	3·93	3·94	3·90	3·93	3·94	3·93	3·98	55·25	7·80	94·29	...
Steel tapped, "	2·87	1·35	2·95	5·471	2·43	2·79	1·02	3·46	51·63 ²	6·02	84·33 ³	...
Steel reduced, "	3·88	3·74	3·78	3·68	3·70	3·78	3·74	3·81	53·07	6·67	88·24	...
Per cent. tapped	72·10	34·20	74·90	...	61·90	70·90	25·60	87·00	93·60	77·30	89·40	...
Per cent. reduced	97·60	95·20	96·00	94·10	94·20	95·90	95·30	96·00	96·19	85·20	93·60	...
Per cent. iron slagged	2·38	4·88	3·97	4·92	5·73	4·08	4·70	4·36	...	14·49	...	6·09
Electrode consumption per ton of steel tapped, kilogrammes.	103·0	89·5	32·8	...	95·07
Electrode consumption per ton of steel reduced, kilogrammes	67·5	66·1	29·3	...	41·63
Kilowatt-hours per kilogramme tapped	5·88	15·50	5·52	...	14·83	6·98	24·6	4·23	...	11·39
" " reduced.	4·34	5·92	4·32	5·86	9·76	9·75	6·75	3·82	...	5·08
" " years per ton tapped.	0·67	1·76	0·63	...	1·69	0·79	2·81	0·48	...	1·30
" " " reduced	0·49	0·67	0·49	0·66	1·11	0·59	0·77	0·44	...	0·57

1 From unreduced charge of the previous experiment.

2 Including 23·6 kilogrammes cleaned out of the furnace, and 2·62 kilogrammes removed after Experiment No. 19.

3 Including steel cleaned out of the furnace.

stant. Because the furnace operated better on a less basic slag than was used in the earlier experiments of Series I., the amount of limestone in the charge was reduced considerably. It is from the results of this series of experiments, Table XXI., that the curves shown in Figs. 6, 7, and 8 have been plotted.

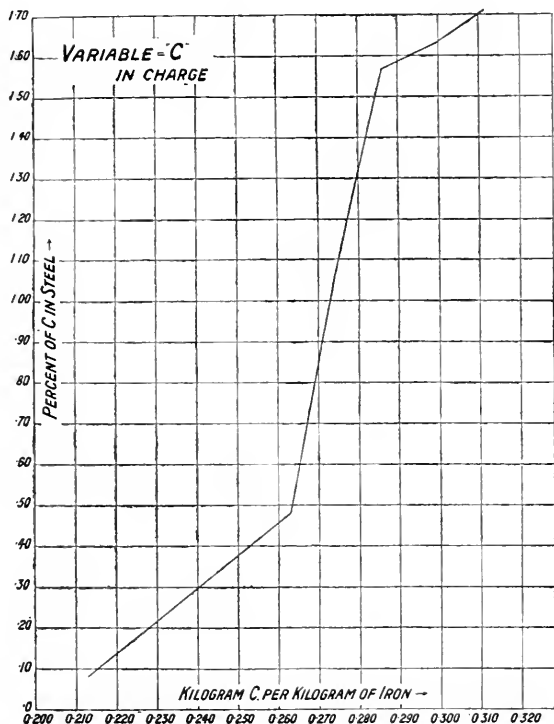


FIG. 6.

SERIES III. *Variation of Limestone in the Charge.*—Four experiments were conducted in which the amount of limestone in the charge was increased successively in experiments until the slag became too basic for tapping, Experiments 14 to 17 inclusive, Table XXI. In Experiment No. 17, 3.18 kilograms of limestone were used, other conditions remaining the same. The furnace operated so poorly with the very basic slag that no metal could be tapped. The amount of coke

charged was based upon the results of Series II., from which it appeared that 0.274 kilogramme of fixed carbon per kilogramme of iron charged should result in the production of a steel containing about 1.00 per cent. carbon. From the results of this series and Experiment No. 10 are plotted the curves shown in Figs. 9 and 10.

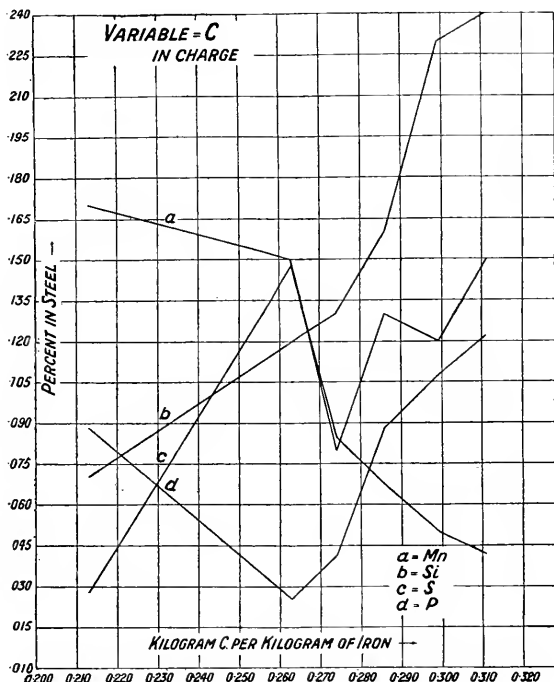


FIG. 7.

SERIES IV. *Variation of Fluorspar in the Charge.*—Five experiments were performed, 18 to 22 inclusive, Table XXI., of which four were successful, in which the amount of fluor-spar in the charge was increased by successive experiments to determine its effect upon the elimination of sulphur by the slag. The amount of coke used was that used in Series III. The lime in the charge was also based upon Series III., but was not all added as limestone, for in each experiment a part

of the limestone was replaced by fluorspar. From the results of this series and Experiment No. 16 the curves shown in Figs. 11 and 12 are plotted.

At the conclusion of Experiment No. 22 the furnace was dismantled and relined. Metal had gradually frozen upon

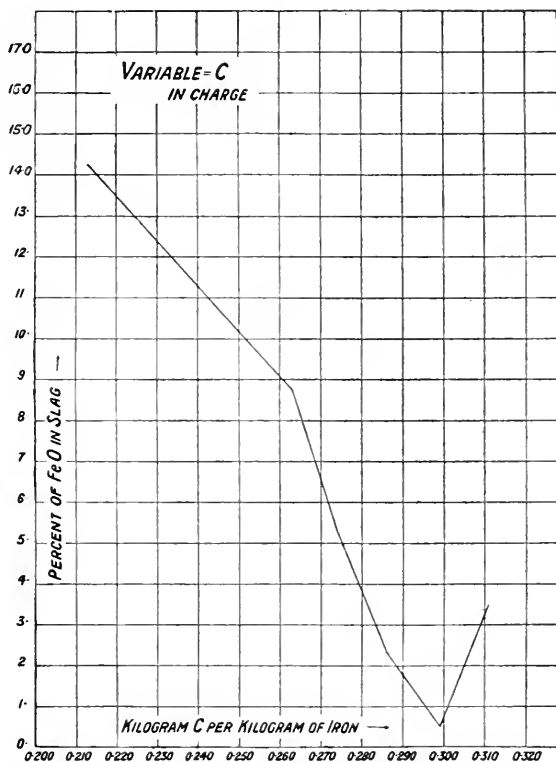


FIG. 8.

the hearth during Experiments Nos. 9 to 22 inclusive, but had not sunk into the hearth to any great extent. The total weight of steel obtained during these fourteen experiments was 51.63 kilogrammes. This includes 23.6 kilogrammes removed from the furnace at the close of Experiment No. 22. The calculated weight of total steel, allowing for no slag loss, was 55.25 kilogrammes. On this basis the percentage ex-

traction for the fourteen experiments was 93.60 per cent. The total weight of steel reduced was 53.07 kilogrammes. Of the metal reduced, 97.28 per cent. was tapped. The calculated weight of steel reduced was 96.19 per cent. of the total calculated steel.

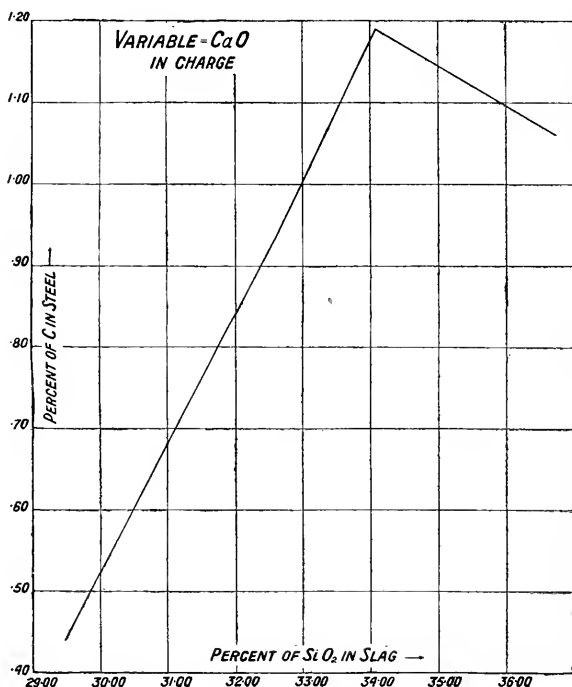


FIG. 9.

SERIES V. *Continuous Experiment No. 23.*—An experiment was made, extending over six hours' running, to note the effect upon the steel of continuous charging and tapping rather than intermittent operation of the furnace, as was done in the other experiments. The power supplied during the experiment was low, which interfered to a great extent with the satisfactory operation of the furnace. One tapping was made about the middle of the experiment, but at the end the furnace froze. The steel removed from the furnace on cooling

was very malleable, but no analysis was made because of the difficulty of taking a representative sample. The charge was based upon the results of the previous intermittent experiments. The slag sample taken was from tappings made throughout the experiment. The furnace shown in Fig. 2 was used for this experiment.

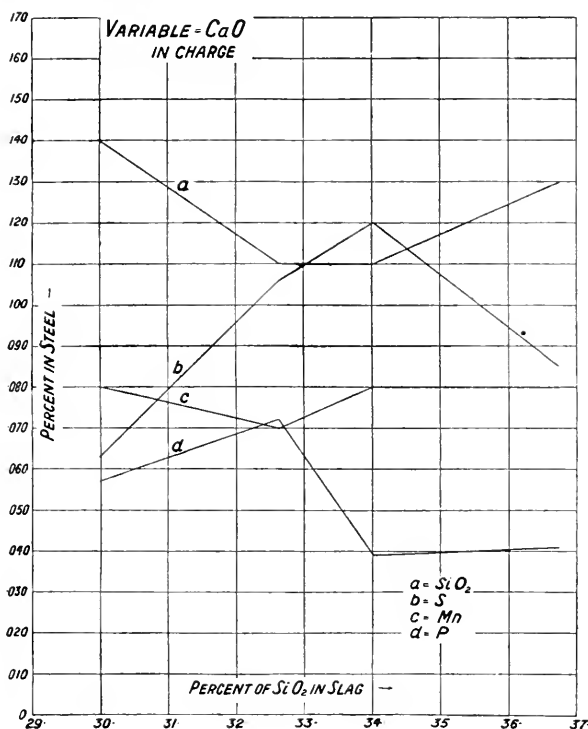


FIG. 10.

Discussion of Results.

Products.—The steels produced varied with the coke in the charge from a soft low carbon steel to a hard high carbon steel. With one exception, they all contained less than 1.75 per cent. carbon. This exception was a white iron containing 2.25 per cent. carbon. The percentage of manganese in the steel was uniform with an average of 0.11 per cent.

The silicon varied to a considerable extent with the basicity of the slag, but could be kept below 0.15 per cent. without difficulty. The average percentage silicon in the steels was 0.12 per cent. The percentages of phosphorus and sulphur

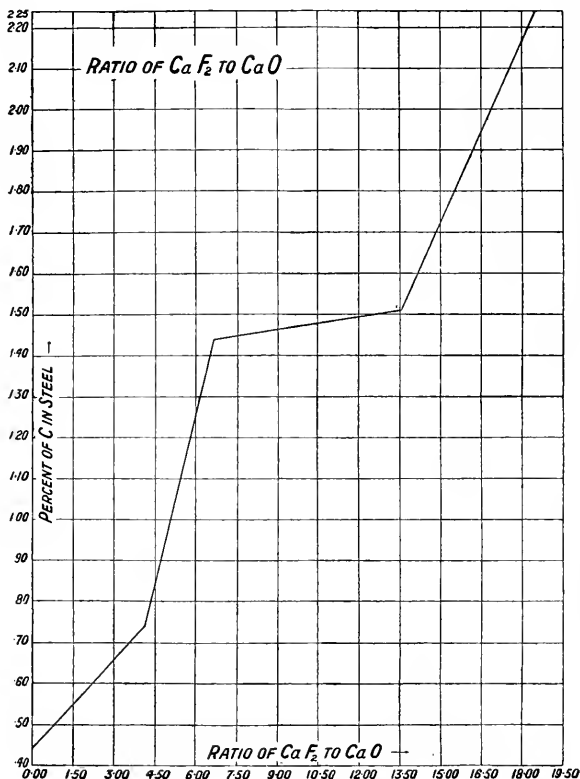


FIG. 11.

in the steels varied under different conditions, which will be discussed later. The loss of iron in the slag was not excessive.

Regulation of Carbon.—From the results obtained, it seems that the regulation of carbon in a steel produced by a direct process is possible within rather close limits.

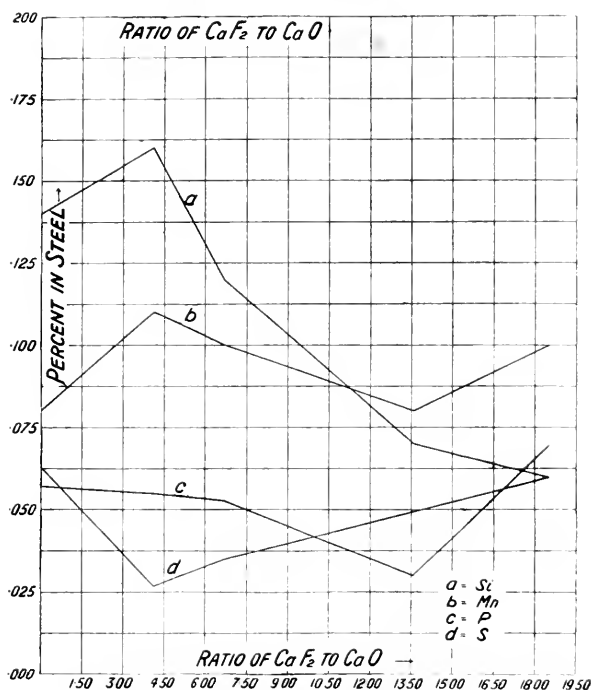


FIG. 12.

TABLE XXII.—Carbon Regulation.

Experiment No.	Carbon in Steel.	Kg. Carbon Charged per Kg. Steel Reduced.	Kg. Carbon Charged per Kg. Steel Reduced, for Reduction.	Kg. CaO Charged per Kg. Steel Reduced.	Kg. CaF_2 Charged per Kg. Steel Reduced.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
3	0.29	0.2810	0.2781	0.6780	...
5	0.33	0.2805	0.2772	0.5490	...
4	0.53	0.2815	0.2762	0.5030	...
9	0.48	0.2745	0.2697	0.3005	...
10	1.06	0.2810	0.2704	0.2940	...
11	1.57	0.2840	0.2683	0.2860	...
12	1.64	0.2920	0.2756	0.2820	...
13	1.71	0.3110	0.2939	0.2875	...
10	1.06	0.2810	0.2704	0.2940	...
14	1.19	0.2895	0.2726	0.3310	...
15	0.92	0.2877	0.2728	0.3361	...
16	0.44	0.2815	0.2851	0.4060	...
18	0.74	0.2877	0.2803	...	0.0132
19	1.44	0.2815	0.2671	...	0.0203
20	1.51	0.2845	0.2694	...	0.0410
21	2.25	0.2785	0.2560	...	0.0542

As shown in Fig. 6, the percentage of carbon in the steel gradually increased with increase of carbon in the charge, up to about 1.50 per cent. in the steel, above which the amount of carbon absorbed by the steel does not increase as rapidly as the increase of carbon in the charge. To determine whether there is any definite relation between the carbon charged and the carbon entering the steel, the results of some of the experiments have been figured to kilogrammes charged per kilogrammes of steel reduced, and from this the amount of carbon entering the metal has been deducted in each case, giving the kilogrammes of carbon actually used per kilogramme of steel reduced, for reduction only.

In Series I. the results of Experiments Nos. 3, 4, and 5 indicate a constant relation between the carbon charged and that entering the steel. The kilogrammes of carbon required per kilogramme of steel reduced for reduction only varied from 0.2781 kilogramme to 0.2762 kilogramme, average 0.2771 kilogramme. The higher figure than that obtained from the results of Series II. was probably due to the charge being more basic.

In Series II. the lime charged was constant, although in calculating it to kilogrammes of steels reduced it appears to be variable because of variation of the amount of steel reduced. From this series for a steel containing from 0.48 per cent. to 1.57 per cent. carbon there appears to be a constant amount of carbon required for reduction only, any added above this amount serving to carburise the steel. This figure varies between 0.2683 kilogramme and 0.2704 kilogramme, average 0.2694 kilogramme. That is, if 0.2694 kilogramme of carbon were charged per kilogramme of steel reduced, theoretically the product would be free from carbon. If 0.2794 kilogramme of carbon were used in the charge, the product would contain 1.00 per cent. carbon. Above 1.57 per cent. of carbon in the steel, the excess of carbon in the charge does not seem to carburise the steel at the same rate.

From the results of Series III., in which the lime in the charge was varied, other factors remaining constant, with the increased lime in the charge there seems to be a gradual increase of carbon required for reduction, and a corresponding

decrease of carbon in the steel (Fig. 9). This is probably due to the formation of calcium carbide with the increased percentage of lime present.

In Series I., Experiments 3, 4, and 5, with increased basicity of the charge, the carbon in the steel decreases, while that used for reduction increases as in Series III. The decrease does not appear so marked with the more basic charge used in Series I. The carbon content of the charge was considerably less than that of Series III.

In Series IV., Fig. 11, the increase of fluorspar in the charge causes a marked increase of carbon in the steel and a corresponding decrease of carbon used for reduction, due probably to the excessive thinning of the slag.

The figures obtained, of course, apply to the particular furnace and charges used, but in a general way the results indicate:—First, that in producing steels containing from 0.25 per cent. to 1.50 per cent. carbon, for any particular furnace and basicity of charge, the carbon content of the steel can be regulated by varying the carbon in the charge; second, that an increase or decrease of lime in the charge causes a corresponding decrease or increase of carbon in the steel; and third, that the use of fluorspar in excessive quantities causes a marked increase in the carburisation of the steel.

Silicon in the Steel.—The results of Series II., Fig. 7, show that with an increased amount of coke in the charge, there is a gradual, although not excessive, increase of silicon passing into the steel. The increased basicity of the charge, Series III., Fig. 10, lowers the percentage of silicon in the steel. Increased charging of fluorspar seems to cause a decrease of silicon in the steel (Series IV., Fig. 12). In general the experiments show that the percentage of silicon in the steel can be kept at a low figure if desired, and that its regulation does not seem difficult.

Phosphorus in the Steel.—Although the ore contained a high percentage of phosphorus (0.124 per cent.), no difficulty was experienced in keeping the percentage in the metal low. In the twenty experiments from 51.70 per cent. to 95.92 per cent. of the total phosphorus charged was slagged, with an average of 77.25 per cent. (Table XXIII.).

In Series II., Fig. 7, the gradual increase of coke in the charge caused an increase of phosphorus in the steel, because of the failure of the phosphorus to pass into the slag as calcium phosphate under the more reducing conditions of operation. Increased lime in the charge (Series III., Fig. 10) seems to result in an increased percentage of phosphorus in the steel. This was probably caused by the more basic slag being too thick for intimate contact with the steel bath

TABLE XXIII.—*Elimination of Phosphorus and Sulphur.*

Experiment No.	Phosphorus in Charge.	Phosphorus in Steel Reduced.	Per Cent. of Phosphorus Slagged.	Sulphur in Charge.	Sulphur in Steel Reduced.	Per Cent. of Sulphur Slagged.
	Grammes.	Grammes.		Grammes.	Grammes.	
1	9.45	2.91	69.20	14.98	0.89	94.05
2	9.48	2.23	76.40	14.98	1.50	89.98
3	9.71	2.07	78.75	16.32	1.82	88.82
4	9.61	2.28	76.40	16.32	1.72	89.42
5	9.55	2.98	68.85	16.32	0.73	95.53
6	9.71	1.10	88.70	16.91	1.88	88.85
8	9.60	0.37	95.92	16.91	1.21	92.85
9	9.52	0.96	89.96	16.32	5.45	66.60
10	9.57	1.16	88.00	16.66	3.21	80.72
11	9.60	3.46	63.90	16.91	2.61	84.57
12	9.66	4.25	56.05	17.26	1.90	89.00
13	9.70	4.70	51.70	17.58	1.67	90.49
14	9.54	1.46	84.70	16.91	4.49	73.40
15	9.55	2.72	71.55	16.91	4.04	76.20
16	9.58	2.16	77.40	16.91	2.31	86.35
18	9.57	2.03	78.80	16.91	1.00	94.18
19	9.57	2.00	79.15	16.91	1.32	92.20
20	9.56	1.12	88.29	16.91	1.83	89.17
21	9.56	2.67	72.15	16.91	2.29	86.42
23	19.29	2.06	89.30	33.14	3.22	96.80
	Average . . .		77.25	Average . . .		87.28

during the agitation caused by the passage of the electric current through it.

Fluorspar, Series IV., Fig. 12, caused a slight decrease of the percentage phosphorus in the steel, when used in small quantity, but when charged in excess, caused the percentage of phosphorus in the steel to increase. The slight thinning of the slag seemed to assist the passage of the phosphorus into the slag. Continuous operation of the furnace did not cause increased phosphorus in the steel.

The conclusions drawn from these results are: First, that increased carbon in the charge causes an increase of the percentage of phosphorus in the steel, because of the stronger reducing conditions; second, increased basicity of the slag does not cause the slagging of more phosphorus if the slag is very thick; third, if a small amount of fluorspar is added to thin the basic slag, the slagging of the phosphorus is assisted; and fourth, continuous operation of the furnace does not cause increased phosphorus in the steel.

Sulphur in the Steel.—The hæmatite used in the experiments contained 0.14 per cent. sulphur and the coke 0.54 per cent. Contrary to expectations, no difficulty was experienced in concentrating the sulphur in the slag. From 66.6 per cent. to 96.8 per cent. of the total sulphur in the charge was slagged, with an average of 87.28 per cent.

In Series II., Fig. 7, the sulphur acted contrary to the phosphorus with the increased reducing atmosphere, being easily slagged, owing to the better conditions for the formation of calcium sulphide. In Series III., Fig. 10, the increase of lime in the charge caused a marked increase in the amount of sulphur passing into the slag. The coke in the charge was low in amount, so that some of the sulphur probably passed into the slag as calcium sulphate. From Series IV., Fig. 12, it seems that a small amount of fluorspar in the charge aids in the elimination of the sulphur from the steel, but an excess causes it to pass into the steel. As in the case of phosphorus, more sulphur passed into the slag when the latter was fluid. Continuous operation of the furnace did not cause increased sulphur in the steel.

The conclusions made are: First, that an increased reducing atmosphere aids in the passage of the sulphur into the slag; second, increased basicity of the slag causes more of the sulphur to be slagged; third, by thinning the slag a small amount of fluorspar assists in sulphur elimination from the steel, but an excess has the contrary effect; and fourth, continuous operation of the furnace does not cause increased sulphur in the steel.

Physical and Metallographic Properties.—The products of all the experiments were either hard or soft, depending upon the

percentage of carbon present, as in the case of steel produced by established methods. The steel from Experiment No. 9 was brittle, caused by the high percentage of sulphur. The steels from Experiments Nos. 19, 20, and 21 were coarsely crystalline on fracture and very brittle. The reason for this is not known. The presence of excess fluorspar in the charge may have affected these properties of the steel.

All of the sections for microscopic examination were taken from the ingot as cast, and were subjected to no further heat treatment before being photographed. They were polished in the usual manner, and etched with picric acid. Studied under the microscope, the steels showed the characteristics of carbon steels. Ferrite and pearlite, or pearlite and cementite, were detected, depending upon the percentage of carbon in the steel (Figs. 13 to 25 inclusive, Plates XV. to XVII.). In only one case was graphite present, in the iron from Experiment No. 21, which contained 2.25 per cent. carbon, and was a white iron.

Slags.

The composition of the slag was affected to a marked degree by the lining of the furnace. A very small amount of lining entering the slags changed their composition considerably from that calculated. During the later experiments this was considered in calculating the slags, but under changing conditions it caused much trouble. The high percentage of magnesia in some of the slags was caused by the magnesite of the lining, while in some experiments, in which the slag attacked the fireclay tile of the roof, the alumina and silica in the slag were increased from this source.

Loss of Iron in the Slag.—The ferrous oxide in the slag was affected by the degree to which the operating conditions were reducing (Fig. 8). With increase of coke in the charge the percentage of ferrous oxide in the slag was decreased, but was little affected by variation of the basicity of the slag. The extremely high results in Experiments Nos. 1 and 2 are due to the carbon in the charge being made slightly less in amount than the calculated, because a very soft steel was desired. The high loss of iron in the slag in Experiment

No. 23 was caused by tappings of slag when unreduced ore was low in the furnace. Some of the unreduced ore passed into the slag. In the operation of such a small furnace continuously this would be a natural result, but should not occur with a large furnace. The slags of all the experiments contained an average percentage of 7.47 per cent. ferrous oxide. The average loss of iron in the slags was 6.09 per cent. With steady operation in a large furnace the loss of iron in the slag should not exceed 4 per cent.

Operation of the Furnace.

The furnace used in these experiments was that shown in Fig. 2, with the exception of Experiment No. 23, when the furnace shown in Fig. 3 was used. The furnace was operated as a combination arc and resistance furnace. The electrodes were regulated so as to be "free burning" as far as possible, that is, with a small space between the ends of the electrodes and the charge, across which a series of small arcs formed. Under these conditions the furnace operated best with 300 amperes and 40 volts, but this was seldom obtained with the varying power delivered at the furnace.

The furnace could be started very readily on a cold charge by lowering the electrodes, starting an arc, and then gradually feeding in charge until a molten mass was formed in the bottom. As the charging advanced the electrodes were gradually raised. The furnace heated up uniformly, and often at the end of an experiment when the charge was all reduced an arc from 3 to 5 inches wide was formed between the flat electrode and the slag. There was a tendency for the molten slag and partially reduced ore to hang along the walls in the back of the electrodes, and until this space had become partially filled up after several experiments there was considerable loss by hanging. At the end of a run, when the last of the cold charge had become molten, there was loss due to excessive boiling out at the top of the furnace. This can be prevented by keeping the top full of cold charge. No difficulty of this nature would be experienced with a shaft furnace. During these experiments metal gradually accumulated upon

the floor of the crucible, but did not sink in to any appreciable extent. This was caused by the variations of the power allowing freezing, and to molten metal being dammed in the furnace after tapping by small ridges and depressions. With a large furnace this loss would not be so noticeable.

The lining of the furnace withstood the action of the basic slags well. During the experiments the furnace was lined twice. The greatest corrosion of the magnesite bricks occurred when the electrodes were too close to the walls in several experiments. The fireclay tile roof gradually became corroded, but water cooling was not necessary, as one set of tiles lasted throughout the experiments.

The conducting hearth was in good condition at the end of the research. It had lowered about three-quarters of an inch during all of the experiments performed in the research. The magnesite packed in around the bars had become a very hard solid mass, having apparently fused and set. The soft iron rods had become crystallised at the upper ends, due to heating and slow cooling, but were intact.

Electrodes.

The flat electrodes gave the desired effect of uniform heating, and permitted the charging of much larger charges than were possible in a furnace previously used with round electrodes, and used about the same amount of power. These electrodes wore uniformly at the ends. Very little regulation of the electrodes was necessary after the first fifteen minutes of any experiment. There was very little tendency for the small arcs to break, although in several experiments short circuits occurred.

The average electrode consumption was 95.07 kilogrammes per ton of steel tapped and 41.63 kilogrammes per ton of steel reduced. In the first case, if the metal cleaned out of the furnace is considered, the electrode consumption closely approaches that per ton of steel reduced. The best results obtained were in Experiment No. 3, in which the consumption was 16.82 kilogrammes per ton of steel tapped and 16.50 kilogrammes per ton of steel reduced, which is a figure which

could probably be attained in a large furnace. The high electrode consumption in some of the experiments was probably caused by small pieces of the electrodes being broken off in manipulation, which would affect the ultimate result more than in large scale operations.

Steel Produced.

A total of 84.33 kilogrammes of steel was produced, including steel cleaned out of the furnace on cooling. This was 89.40 per cent. of the total calculated weight of steel. The calculated weight of the steel reduced was 88.24 kilogrammes which was 93.60 per cent. of the total calculated steel.

Energy Consumption.

The average energy consumption per kilogramme of steel tapped, not including steel cleaned out of the furnace, was 11.39 kilowatt-hours, or 1.30 kilowatt-years per ton. The average energy consumption per kilogramme of steel reduced was 5.03 kilowatt-hours, or 0.57 kilowatt-years per ton. The best results obtained in a single run were in Experiment No. 23, when the energy used was 4.23 kilowatt-hours per kilogramme of steel tapped, 3.82 kilowatt-hours per kilogramme of steel reduced, 0.48 kilowatt-years per ton tapped, and 0.44 kilowatt-years per ton reduced. Although the power supplied was very unsteady during work, the power consumption was very low, due probably to the continuous operation of the furnace. With a large furnace operating continuously the power consumption should be reduced to 0.30 kilowatt-years per ton of steel tapped, or 2.65 kilowatt-hours per kilogramme.

Continuous Process for the Production of Steel directly from Ore in the Electric Furnace.

To produce a steel directly from ore in the electric furnace at a cost low enough to compete with the present methods of steel manufacture, a process must have possibilities of large output. This can best be accomplished in an electric shaft furnace somewhat similar to the blast-furnace. In a con-

tinuous furnace of this type the energy consumption can be kept at a lower figure than in an intermittent furnace, because of the use of the gases for pre-heating and reduction of the charge.

As a result of the continuous experiment of short duration made in this research, from the results of which it appears that there should be no greater difficulty in the elimination of impurities from the steel than in intermittent operation of the furnace, the following process is proposed for the direct production of steel from ore in a continuous electric furnace. The charge of ore, flux, and reducing agent is charged continuously into an electric shaft furnace. A low carbon steel is tapped from the crucible into a large mixer, in which the steel is carburised to the desired point and treated with ferro-alloys. If the production of a low carbon steel is attempted by reducing the carbon in the charge to a very low point above that required theoretically, there will be excessive loss of iron by slagging. To avoid this loss, advantage is taken of the fact that the greater part of the reduction in the electric furnace of the shaft type is performed by solid carbon in the upper part of the crucible. In the continuous experiment performed it was noticed that, in spite of the presence of an amount of carbon in the charge sufficient to reduce the ore, if the partially reduced charge came in contact with the already reduced metal there was decarburisation of the steel. To get this condition the furnace could be operated in this manner. When a sufficient amount of metal has accumulated in the crucible for tapping, the slag accumulated above it is tapped from a tap hole at a higher level than the metal tap hole. The partially reduced charge from above then drops upon the metal, and decarburisation takes place. At the end of the decarburisation period, determined by experience, the metal is tapped into the mixer for further treatment, from which it may be cast into ingots.

For the proper accomplishment of this process a higher temperature would be necessary than that attained in the ordinary pig iron electric shaft furnace, because of the higher melting point of the steel. Also advantage in purifying the steel would be obtained by agitation of the steel by passage of

the current through it. It is believed that these results can be accomplished in a furnace of the type shown in Fig. 5.

This furnace consists of a crucible with a shaft superimposed upon it, and is of rectangular cross section. There are two flat electrodes of graphite or carbon, extending the length of the furnace, which are surrounded by water jackets. These electrodes are made of carbon or graphite plates, of the proper size for the current to be carried and set side by side. They may be grooved to lessen the formation of small arcs. The bottom of the hearth is conducting, and consists of iron rods imbedded in magnesite. Each of these electrodes is connected to a phase of a three-phase circuit, in the delta connection. By this arrangement uniform heating of the charge in the crucible is insured, for the current passes between the two graphite electrodes at the top of the crucible, and down the sides between each of the upper electrodes and the conducting hearth. This would also cause agitation of the metal.

A furnace of this type can be easily increased in size by increasing the length, making a furnace similar to the long rectangular Matheson copper blast-furnace, which has operated so successfully. The electrodes would then be long plates, comparatively thin in contrast to the tremendous thickness and diameter the electrode of square or round cross section would assume in a circular furnace of large capacity.

Cost of Production of Steel directly from Ore.

In figuring the cost of production of steel directly from ore in the electric furnace, the cost of materials and labour is taken as near as possible to that prevailing in the United States. The charge is proportioned according to Experiment No. 16, on a basis of 95.0 per cent. extraction of the iron. The ore, coke, limestone, and fluorspar are of the analysis used in the experiments. The cost of erection of the power plant is not considered in the capital charge.

Conclusions.

The following conclusions are made as a result of the experiments performed:—First, the production of a steel of

variable percentage carbon directly from ore in the electric furnace can be accomplished; second, it is possible to regulate the carbon in the steel by varying the amount of carbon charged; third, in spite of the presence of considerable phosphorus and sulphur in the charge, a steel can be produced containing percentages of each below the limit set by the

TABLE XXIV.—*Cost of Production of Steel directly from Ore.*

	Power, \$25 per Kilowatt- Year.	Power, \$20 per Kilowatt- Year.	Power, \$15 per Kilowatt- Year.	Power, \$10 per Kilowatt- Year.
	\$	\$	\$	\$
1820 kilogrammes hæmatite at \$3·00 per ton	5·46	5·46	5·46	5·46
342 kilogrammes coke at \$2·00 per ton	0·68	0·68	0·68	0·68
725 " " limestone at \$1·00 per ton	0·73	0·73	0·73	0·73
7·6 kilogrammes fluorspar at \$9·00 per ton	0·07	0·07	0·07	0·07
0·30 kilowatt-years	7·50	6 00	4·50	3·00
16·5 kilogrammes graphite electrode 12 cents per kilogramme	1·98	1·98	1·98	1·98
Labour and maintenance	2·00	2·00	2·00	2·00
Capital charges	1·25	1·25	1·25	1·25
General expenses	0·25	0·25	0·25	0·25
Additions, &c.	0·50	0·50	0·50	0·50
Total	\$20·42	\$18·92	\$17·42	\$15·92

consumers; fourth, the steel may be produced in a furnace operating intermittently or continuously; fifth, silicon in the steel may be kept low if desired by use of a basic slag; sixth, used in small quantities fluorspar assists in the slagging of impurities, but used in excess it has the contrary effect and causes increased percentage of carbon in the steel; and seventh, the loss of iron in the slag need not exceed 4·00 per cent. of the total iron charged.

THE PRODUCTION OF CHROMIUM STEEL DIRECTLY FROM ORE IN THE ELECTRIC FURNACE.

Experiments.

The experiments upon the production of chromium steel directly from ore in the electric furnace were conducted in a

manner similar to the experiments already described, with the exception that chromite was added to obtain the desired percentage of chromium in the steel. The compositions of the coke, limestone, and fluorspar used are given in Table XX. The chromite and lime were of the composition given in Table XXV.

TABLE XXV.—*Chromium Steel. Raw Materials.*

	Chromite, per Cent.	Lime, per Cent.
Cr ₂ O ₃	46.35 (31.7 Cr)	...
FeO	21.45 (16.6 Fe)	...
SiO ₂	5.48	1.34
Al ₂ O ₃	12.80	1.90 (AlO and FeO)
MgO	10.08	trace
CaO	trace	92.76
Phosphorus	0.013	0.06
Sulphur	0.45	...

The experiments were performed in the furnace shown in Fig. 2. This furnace was operated in a manner similar to the operation of the double electrode furnace with the electrode free burning.

The charges in these experiments were varied to give chromium steels of different percentages of chromium, but the desired results were not accomplished owing to chromium left in the furnace from the previous experiments upon ferro-chrome entering the steel. The slag was affected in a similar manner, so that no calculation can be made regarding the loss of chromium in the slag. The condensed results of these experiments are in Table XXVI.

The presence of chromium in the charge seems to have caused a marked increase of carbon in the steel. The amount of carbon charged was slightly less than that used in producing a 0.40 per cent. carbon steel. In none of the experiments was this percentage of carbon closely approached.

The percentage of phosphorus was high in all of the experiments except No. 27, while the percentage of sulphur was low in all experiments except No. 27. The percentage of silicon in the steel varied between 0.11 and 0.29 per cent. It is believed that by careful regulation of operating conditions the phosphorus and sulphur in the steel could be reduced.

The ingots cast were, as a rule, more solid and more free from blowholes than the carbon steel ingots. The metal was hard and slightly brittle. The sections for microscopic study were etched with dilute hydrochloric acid. They showed the characteristic double carbide of iron and chromium of chromium steels (Figs. 26 to 30 inclusive, Plate XVII.).

TABLE XXVI.—*Production of Chromium Steel directly from Ore.*

Experiment No.	24	25	26	27	28	Average.
Charge—						
Haematite, kilogrammes . .	4.54	4.54	4.54	4.54	4.54	...
Chromite, "	0.91	0.91	0.68	0.45	0.23	...
Coke, "	0.94	0.96	0.94	0.91	0.88	...
Lime, "	1.14	1.14	1.02	1.02	1.02	...
Fluorspar, "	0.057	0.057	0.057	0.057	0.057	...
Products—						
Steel, Chromium, per cent. .	10.94	8.83	14.38	8.00	5.52	...
" Carbon, "	1.62	1.56	2.03	1.74	1.99	...
" Silicon, "	0.22	0.19	0.25	0.11	0.29	...
" Phosphorus, "	0.093	0.123	0.117	0.039	0.145	...
" Sulphur, "	0.021	0.021	0.021	0.069	0.014	...
Slag, SiO ₂ , "	29.20	30.80	30.32	25.92	25.68	...
" Cr ₂ O ₃ , "	11.43	13.51	13.20	13.04	12.40	...
" CaO, "	24.81	24.50	32.30	32.60	34.60	...
" MgO, "	14.02	10.53	7.18	9.80	7.23	...
" FeO, "	7.29	8.50	3.79	3.51	2.91	...
" Al ₂ O ₃ , "	3.99	4.50	5.63	5.30	7.97	...
Calculated percentage chromium (approximate)	9.20	9.50	6.49	4.83	2.45	...
Kilog. carbon per kilog. Fe and Cr	0.252	0.258	0.262	0.265	0.265	...
Calculated steel, kilogrammes	3.14	3.05	3.24	2.95	2.86	...
Steel tapped, "	2.73	1.79	2.61	2.28	2.16	11.7
Percentage, tapped	86.90	58.70	80.04	77.10	75.30	75.00
Electrode consumption, per ton, tapped, kilogrammes	45.4	69.7	47.4	54.2	57.3	54.8
Kilowatt-hours per kilog., tapped	4.38	5.32	3.02	2.74	4.38	3.97
" years per ton, tapped	0.59	0.61	0.34	0.31	0.50	0.45

Conclusions.

From these experiments the following conclusions are drawn: First, that a chromium steel can be made in the electric furnace directly from haematite and chromite; second, the control of carbon in the product by means of the carbon charged is difficult if chromium is present; and third, the elimination of sulphur, phosphorus, and silicon in the steel by careful regulation of the charge is possible.

THE PRODUCTION OF MOLYBDENUM STEEL DIRECTLY FROM ORE IN THE ELECTRIC FURNACE.

Experiments.

Three experiments were conducted to try the possibilities of the production of molybdenum steel directly from hæmatite and molybdenite in the electric furnace, using lime as a means of slagging the sulphur as calcium sulphide. The results are somewhat unsatisfactory as regards the elimination of sulphur from the steel, because of the fact that in previous experiments allowance was made for the lining entering the slag in calculating the charge, but in this case the lining did not influence the slag to so great an extent. As a result the metal obtained contained a high percentage of sulphur. Further experiments could not be made because of lack of molybdenite. The composition of the hæmatite and fluorspar used is given in Table XX. and the lime in Table XXV. The molybdenite had the following percentage composition:—

	Per Cent.
Molybdenum	47.50
Iron	1.23
Silica	13.90
Phosphorus	6.608
Sulphur	30.64

The results of the experiments (Table XXVII.) indicate that while a molybdenum steel can be made directly from hæmatite and molybdenite in an electric furnace of the arc type (Fig. 2), the losses of molybdenum are excessive. The average loss of molybdenum in the slag was 20.7 per cent., and that unaccounted for, which is considered as volatilised, was 25.4 per cent.: total, 46.7 per cent. This loss occurred in spite of the operation of the furnace as far as possible as a resistance furnace. It is probable that the loss of molybdenum could be reduced either by performing the reduction in a resistance furnace which permitted close regulation of temperature or by reducing the hæmatite first in an arc furnace, dipping the electrode into the slag, and then charging the molybdenite with a proper mixture for reduction and removal of the sulphur. The iron loss in the slag was high, due to the low

amount of carbon charged in an effort to keep the carbon in the steel at a low percentage. The presence of molybdenum in the charge does not cause a high percentage of carbon in the steel, as was the case with chromium. There was no

TABLE XXVII.—*The Production of Molybdenum Steel directly from Ore.*

Experiment No.	29	30	31	Average.
Charge—				
Hæmatite, kilogrammes	4.54	4.54	4.54	...
Molybdenite, "	0.45	0.39	0.23	...
Coke, "	0.90	0.90	0.90	...
Lime, "	1.35	1.48	1.48	...
Fluorspar, "	0.057	0.114	0.114	...
Products—				
Steel, Molybdenum, per cent.	3.52	5.38	2.62	...
" Carbon, "	0.30	0.50	0.46	...
" Silicon, "	0.04	0.10	0.14	...
" Phosphorus, "	0.027	0.058	0.036	...
" Sulphur, "	0.895	0.560	0.720	...
Slag, MoO ₃ , "	1.21	0.42	1.30	...
" SiO ₂ , "	40.96	45.44	40.72	...
" CaO, "	28.80	28.45	28.55	...
" MgO, "	4.98	8.58	10.14	...
" FeO, "	11.19	11.53	8.75	...
" Al ₂ O ₃ , "	13.55	5.62	11.56	...
Calculated percentage molybdenum in steel (approximate)	7.75	6.68	3.96	...
Kilog. carbon per kilog. Fe and Mo	0.252	0.264	0.271	...
Calculated steel, kilogrammes	2.76	2.78	2.70	...
Steel tapped, "	1.82	2.27	2.30	...
Steel reduced, "	2.16	2.30	2.32	...
Per cent. tapped	60.9	81.8	85.2	75.9
" reduced	78.1	82.8	86.1	82.3
" iron slagged	17.84	16.39	12.61	15.6
" molybdenum slagged	16.32	7.01	33.8	20.7
" molybdenum volatilised	47.7	24.8	3.7	25.4
Total percentage loss of molybdenum	64.0	31.8	42.5	46.1
Electrode consumption per ton of steel tapped, kilogrammes	65.9	52.9	52.1	56.9
Electrode consumption per ton of steel reduced, kilogrammes	55.5	52.1	51.7	53.1
Kilowatt-hours per kilogramme steel tapped	6.69	4.12	4.10	4.97
" " " " reduced	5.67	4.06	3.51	4.41
" " " " steel tapped	0.76	0.47	0.47	0.56
" " " " reduced	0.64	0.46	0.40	0.50

difficulty in keeping the phosphorus and silicon low in the steels.

The ingots cast were solid and free from blowholes, but were very brittle. The sections for microscopic study were etched with picric acid, being taken as cast (Figs. 31 to 33 inclusive, Plate XVIII.).

Considering the extreme acidity of the slags in these experiments, all above 40·0 per cent. silica, there can be little doubt of the possibility of almost complete slagging or volatilisation of the sulphur with a charge containing a very high amount of lime, so that it should be possible to produce a steel containing less than 0·10 per cent. sulphur.

TABLE XXVIII.—*Elimination of Sulphur from the Steel.*

Experiment No.	Sulphur Charged. Grammes.	Sulphur in Steel. Grammes.	Sulphur Slagged. Per Cent.
29	175·23	1·94	98·60
30	131·19	1·29	98·50
31	81·71	1·67	98·20

Conclusions.

From the preceding experiments it is concluded:—First, that a molybdenum steel can be produced directly from hæmatite and molybdenite in the electric furnace, with lime as a desulphurising agent, but that in an arc furnace the losses of molybdenum are high if the molybdenite is mixed with the hæmatite and the rest of the charge for smelting together, although this might be overcome by adding the molybdenite at the end of the reduction; second, if desired, the percentage carbon in the steel can be kept at a low figure, but high losses of iron and molybdenum occur; and third, impurities can be readily slagged off with an excess of lime in the charge.

THE PRODUCTION OF TUNGSTEN STEEL DIRECTLY FROM ORE IN THE ELECTRIC FURNACE.

Experiments.

In previous experiments on the direct production of tungsten steel from ore in the electric furnace, difficulty was experienced by the author in making a steel low in carbon

and free from large amounts of sulphur. The experiments following (Table XXIX.) were made with these points particularly in view. The furnace used throughout the experiments was that shown in Fig. 2. The composition of the hæmatite, coke, and fluorspar used is given in Table XX.,

TABLE XXIX.—*The Production of Tungsten Steel directly from Ore.*

Experiment No.	32	33	34	35	Average.
Charge—					
Hæmatite, kilogrammes	4.54	4.54	4.54	4.54	...
Ferberite, "	0.45	0.45	0.45	0.45	...
Coke, "	0.85	0.85	0.85	0.85	...
Lime, "	0.94	0.94	0.94	0.94	...
Fluorspar, "	0.028	0.028	0.028	0.028	...
Products—					
Steel, Tungsten, per cent. . . .	3.69 ¹	4.94	7.11	3.60	...
" Carbon, "	1.75	0.35	0.27	0.18	...
" Manganese, "	0.15	0.10	0.07	0.05	...
" Silicon, "	0.10	0.12	0.11	0.07	...
" Phosphorus, "	0.024	0.023	0.033	0.021	...
" Sulphur, "	0.022	0.050	0.028	0.027	...
Slag, WO ₃ , "	2.53	3.42	3.20	3.09	...
" SiO ₂ , "	24.64	27.86	26.52	26.31	...
" CaO, "	26.70	21.85	24.95	8.75	...
" MgO, "	15.64	16.67	18.74	21.25	...
" FeO, "	11.08	11.65	9.35	15.65	...
" Al ₂ O ₃ , "	9.29	15.64	13.04	10.63	...
Calculated percentage tungsten in steel (approximate)	7.38	7.39	7.24	7.50	...
Kilog. carbon per kilog. Fe and W. . . .	0.238	0.238	0.238	0.238	...
Calculated steel, kilogrammes	2.85	2.84	2.90	2.80	...
Steel tapped, "	0.71	1.25	1.82	3.20 ²	...
Steel reduced, "	2.50	2.53	2.55	2.42	...
Percentage tapped	25.00	44.00	62.70
" reduced	87.5	89.05	87.98	86.30	87.72
" iron slagged	10.42	8.20	9.48	10.34	9.61
" tungsten slagged	31.45	42.25	42.50	47.50	40.90
Kilowatt-hours per kilog. steel tapped	11.78	7.18	...	9.48
" " " " reduced	5.8	5.12	4.44	5.12
" years per ton steel tapped	1.34	0.82	...	1.08
" " " " reduced	0.66	0.58	0.51	0.58

and the lime in Table XXV. Ferberite concentrates from Boulder Co., Colorado, which were of the following percentage composition, were used for the addition of tungsten:—WO₃, 58.72 (46.6 tungsten); FeO, 30.08 (23.40 iron); MnO, 2.55 (1.84 manganese); SiO₂, 4.86; CaO, 3.46; phosphorus, 0.34; and sulphur, 0.20.

At the conclusion of Experiment No. 35 the furnace was

¹ Poor sample.² From previous experiment.

3

cleaned out and relined. The total weight of steel obtained in these experiments was 9.77 kilogrammes, including 2.79 kilogrammes removed from the furnace after the last run. Of a calculated weight of steel of 11.39 kilogrammes, 10.01 kilogrammes were reduced, or 87.9 per cent. Of the total calculated weight of steel, 86.4 per cent. was tapped, and 96.8 per cent. of the steel reduced was tapped.

From the results obtained, it seems that if an attempt is made to regulate the carbon in the steel by the amount of carbon charged, that the carbon in the steel may be kept at a low percentage, but there is a high loss of tungsten in the slag. The iron loss in the slag was also high. No difficulty was experienced in causing the silicon, phosphorus, and sulphur to pass into the slag. The power consumption was high, but it was probably due to irregularity of the power supplied during the experiment.

The ingots cut were somewhat filled with blowholes, but were very tough and not brittle. Sections for microscopic study were taken as cast, and after etching with picric acid, show the characteristics of low carbon tungsten steel (Figs. 34 to 36 inclusive, Plate XVIII.).

Conclusions.

The following conclusions are drawn:—First, that if the percentage carbon in the steel is regulated to give a steel of low carbon content by decreasing the carbon in the charge, there will be a high loss of iron and tungsten in the slag; second, that there should be no difficulty in keeping the impurities in the steel at a low point.

THE PRODUCTION OF FERRO-CHROMIUM DIRECTLY FROM CHROMITE IN THE ELECTRIC FURNACE.

Experiments.

Seven experiments were made upon the production of ferro-chromium directly from chromite in the electric furnace with carbon as the reducing agent. The results of these experiments are given in Table XXX. The furnace shown in Fig. 2 was

TABLE XXX.—The Production of Ferro-chromium directly from Ore.

Experiment No.	36	37	38	39	40	41				42			
Charge:—						a	b	c	d	e	f	a	b
Chromite, kilogrammes	4.54	4.54	4.54	4.54	4.54	27.24	18.16
Coke, "	0.85	0.85	0.85	0.74	0.62	5.10	3.68
Lime, "	0.57	0.57	0.57	0.57	0.57	3.05	2.04
Fluorspar, "	0.037	0.057	0.057	0.057	0.057	0.31	0.20
Product alloy:—													
Chromium, per cent.	51.80	48.60	49.70	52.70	57.10	50.69	68.20	58.90	56.10	68.00	67.10	62.60	72.70
Carbon, "	10.05	8.74	11.50	3.72	9.28	6.50	9.31	8.72	7.89	4.32	7.40	5.28	8.32
Silicon, "	0.81	1.10	1.26	0.87	0.35	0.67	0.60	1.23	1.25	0.96	1.03	0.79	0.56
Phosphorus, "	0.128	0.133	0.110	0.106	0.120	0.106	0.099	0.108	0.119	0.106	0.106	0.121	0.119
Sulphur, "	0.073	0.038	0.096	0.061	0.085	0.071	0.105	0.055	0.016	0.031	0.054	0.020	0.023
Slag, CrO ₃ , "	8.03	7.57	6.96	8.98	8.81	9.15	12.60	10.72	13.43	13.13	13.34	8.78	11.40
" SiO ₂ , "	23.40	24.60	23.40	20.25	26.60	32.60	34.20	29.20	28.00	28.90	28.00	36.84	30.50
" FeO, "	9.02	7.29	18.96	15.10	10.17	6.10	14.82	15.43	14.81	15.17	17.55	8.73	16.99
Calculated percentage chromium (approx.).	65.50	65.50	65.50	65.50	65.50	65.50	65.5
Kilogs. carbon per kilog. iron and chromium	0.312	0.312	0.312	0.271	0.228	0.418
Calculated alloy, kilogrammes	2.02	1.82	2.03	1.76	2.28	13.36	8.88
Alloy tapped, "	1.59	2.22	2.34	1.11	1.21	1.21	0.97	1.48	1.48	1.48	1.59	0.68	1.14
Per cent. tapped	78.50	82.90	86.30	62.95	53.30	Total tapped, 8.21 kilog., 61.8 per cent.				Total tapped—			
Electrode consumption per ton tapped, kilogs.	105.0	75.00	71.20	102.3	94.6	24.10	81.50
Kilowatt-hours per kilogramme alloy tapped.	7.00	6.02	5.68	14.01	10.38	6.63	8.00
Kilowatt-years per ton alloy tapped	0.79	0.68	0.65	1.78	1.18	0.76	0.91

used in the experiments. The analyses of the chromite, coke, lime, and fluorspar are given in Tables XX. and XXV.

Five experiments were made in which the furnace was charged and tapped upon the completion of reduction. In these experiments the chromium percentage of the alloy seemed to run considerably lower than the theoretical calculation, although this is accounted for in a measure by the fact that the carbon in the metal was not considered in calculating the theoretical percentage. The carbon was high in all of the alloys, and does not seem to be influenced by the carbon in the charge as long as there is excess. Phosphorus was high in all of the alloys. The operating conditions were probably not oxidising enough for its removal as the sulphate. The ore contained considerable sulphur, but the sulphur was slagged off readily under the strong reducing conditions as calcium sulphide. There was considerable loss of chromium and iron in the slag. In some cases the percentage of iron in the slag exceeded that of chromium, but in no cases did the percentage of chromic oxide in the slag exceed 9 per cent.

In the continuous experiments, Nos. 41 and 43, the percentage of chromium in the alloy closely approaches the theoretical. The percentage carbon was also lower in these alloys because of the decarburising effect of the unreduced oxide present. The slag loss of iron and chromium was higher in these runs than in the intermittent experiments, because of unreduced oxide getting into it on tapping.

A total of 22.59 kilogrammes of ferro-chrome was tapped during the experiments, or an average extraction of 69.5 per cent. The average electrode consumption was 79.1 kilogrammes per ton of metal tapped. The average power consumption was 8.26 kilowatt-hours per kilogramme or 0.94 kilowatt-year per ton.

The alloys cast were brittle and hard when low in chromium and high in carbon, but when high in chromium and low in carbon were so brittle and soft that no sections could be made. The sections, as cast, etched with dilute hydrochloric acid, showed the characteristic double carbide of chromium and iron (Figs. 27 to 41 inclusive, Plates XVII. to XIX.).

Conclusions.

The following conclusions are made: First, that ferro-chromium can be easily manufactured directly from chromite in the electric furnace; second, that the percentage of carbon in the ferro-chromium cannot be kept low by regulating the carbon charged without excessive loss of chromium in the slag; third, that the percentage carbon in the ferro-chromium must be regulated by decarburisation with an oxide slag of iron or chromite after tapping off the slag from reduction; fourth, that silicon and phosphorus cannot be kept low in the alloy under the strong reducing conditions necessary; and fifth, that sulphur can be easily made to pass into the slag.

THE PRODUCTION OF FERRO-MOLYBDENUM DIRECTLY FROM
ORE IN THE ELECTRIC FURNACE.

Experiment.

An experiment was made, No. 43, to test the possibility of sulphur elimination with a charge containing excess lime and carbon as a reducing agent. The experiment was made directly after the experiments on molybdenum steel, and cannot be considered as quantitative as the furnace lining was in poor condition. Some iron was left in the furnace which diluted the product. The molybdenite was of the same composition as that used in the production of molybdenum steel. The analyses of the coke and fluorspar are given in Table XX., the lime in Table XXV. The furnace shown in Fig. 2 was used for the experiments, and was operated as a resistance furnace.

CHARGE.						Kilogrammes.
Molybdenite	1.82
Coke	0.47
Lime	1.37
Fluorspar	0.114

FERRO-MOLYBDENUM.						Per Cent.
Molybdenum	50.55
Carbon	6.73
Silicon	0.94
Phosphorus	0.078
Sulphur	0.19

	SLAG.
MoO	3.18
CaO	41.80
MgO	12.75
FeO	7.56

On tapping, 0.68 kilogrammes of ferro-molybdenum were obtained. The odour of sulphur was very noticeable during the experiment. The product was very brittle. The section was etched with pieric acid (Plate VI., Fig. 42). The sulphur in the alloy was much lower than in the molybdenum steels because of the more basic charge.

Conclusions.

It may be concluded: First, that ferro-molybdenum can be made directly from molybdenite in the electric furnace, with excess lime as a desulphurising agent and carbon as a reducing agent; second, that a product of low percentage carbon may be made; and, third, that sulphur can be readily slagged as calcium sulphide with a charge of excess lime.

THE PRODUCTION OF FERRO-TUNGSTEN DIRECTLY FROM ORE IN THE ELECTRIC FURNACE.

Experiments.

Seven experiments were made upon the direct production of ferro-tungsten from ferberite. The furnace used was similar to that shown in Fig. 1, but of one half the internal dimensions. The ferberite was that used for the tungsten steel experiments. The analysis of the coke is given in Table XX., the lime in Table XXV., the hæmatite in Table XII., and the fluorspar was pure calcium fluoride.

In each experiment a decarburising slag was added to the furnace when reduction of the charge was completed, and allowed to act for from ten to twenty minutes. It was tapped from the furnace with the ferro-tungsten, and the slag from reduction.

As shown in Table XXXI., the alloys obtained, with two exceptions, run somewhat lower in tungsten than was calculated. This was caused by three conditions: first, the

presence of iron from a previous run hanging in the furnace; second, loss of tungsten in the slag; and third, the iron reduced from the decarburising slag. The carbon of all of the alloys was low for ferro-tungsten. It is believed that this was assisted considerably by the use of the decarburising slag of iron oxide and lime, and that with a longer decarburisation period

TABLE XXXI.—*The Production of Ferro-tungsten directly from Ore.*

Experiment No.	44	45	46	47	48	49	50
Charge—							
Ferberite, kilogrammes	2.27	4.54	2.27	2.27	2.72	2.72	2.72
Hæmatite, „	0.68	1.36	0.68	0.68
Coke, „	0.57	1.25	0.62	0.69	0.51	0.51	0.51
Lime, „	0.34	0.71	0.41	0.43	0.34	0.34	0.34
Fluorspar, grammes	0.028	0.057	0.028	0.028	0.028	0.028	0.028
Refining slag—							
Hæmatite, kilogrammes	0.34	0.34	0.34	0.34	0.34	0.34	0.34
Lime, „	0.09	0.09	0.09	0.09	0.09	0.09	0.09
Fluorspar „	20.00	20.00	20.00	20.00	20.00	20.00	20.00
Product—							
Alloy, Tungsten, per cent. . . .	38.74	49.64	41.39	43.35	42.19	37.50	59.01
„ Carbon, „	1.77	1.82	2.05	2.51	1.66	2.04	2.02
„ Manganese, „	0.32	0.16	0.42	0.38	0.16	0.33	0.16
„ Silicon, „	0.47	0.31	0.24	0.44	0.14	0.07	0.09
„ Phosphorus, „	0.044	0.046	0.042	0.048	0.051	0.054	0.020
„ Sulphur, „	0.032	0.068	0.089	0.017	0.014	0.021	0.015
Slag, WO_3 , „	8.64	4.14	7.20	4.24	4.00	5.28	4.88
„ SiO_2 , „	30.12	31.10	31.00	31.40	30.40	29.28	29.64
„ CaO , „	21.30	37.00	30.00	24.60	28.00	21.10	29.30
„ MgO , „	12.60	12.00	19.60	26.64	24.48	23.64	18.80
„ FeO , „	12.10	5.70	5.84	4.52	5.84	5.10	6.87
„ Al_2O_3 , „	11.09	8.70	5.24	6.95	6.22	11.67	7.88
Calculated per cent. W in alloy (approx.) .	50.00	50.00	50.00	50.00	65.00	65.00	65.00
Kilogrammes carbon per kilog. W and Fe	0.202	0.222	0.222	0.212	0.214	0.214	0.214
Calculated alloy, kilogrammes	2.30	4.60	2.30	2.30	1.95	1.95	1.95
Alloy tapped, kilogrammes	0.91	3.98	2.56	1.02	2.96	1.02	2.10
Per cent. tapped	39.50	86.30	...	44.2	...	52.4	...
Electrode consumption per ton tapped, kg.	...	83.8	65.1
Kilowatt-hours per kilogramme tapped .	10.50	5.75	4.40	12.70	4.10	11.54	4.30
Kilowatt-years per ton tapped	1.19	0.66	0.50	1.44	0.47	1.34	0.49

the carbon in the alloy could be reduced still further. The greater part of the manganese in the charge was either slagged or volatilised. The percentage of silicon was high in some of the products, but was much lower when there was no iron ore in the charge. Phosphorus and sulphur were easily slagged in spite of a high percentage of both in the ore. The slags contained from 4.66 to 8.64 per cent. tungstic oxide and ferrous oxide in about the same percentage.

During the experiments 14.55 kilogrammes of ferro-tungsten were made, or an extraction of 83.8 per cent. The electrode consumption for the two experiments in which it was determined averaged 74.45 kilogrammes per ton. This figure could easily be reduced on larger scale operations. The average energy consumption for the seven experiments was 7.61 kilowatt-hours per kilogramme tapped, or 0.87 kilowatt-years per ton.

The ferro-tungsten was hard and brittle. The castings were free from blowholes. Sections, as cast, were etched with picric acid, and showed the characteristic double carbide of iron and tungsten (Figs. 43 to 48 inclusive, Plate XX.).

Conclusion.

The following conclusions are made :—First, ferro-tungsten can be produced directly from ferberite in the electric furnace; second, by the use of decarburising slag before tapping, the percentage of carbon in the alloy can be kept below 2.00 per cent; third, manganese, silicon, phosphorus, and sulphur do not enter the ferro-alloy in high percentages; and fourth, the loss of tungsten by slagging need not be excessive.

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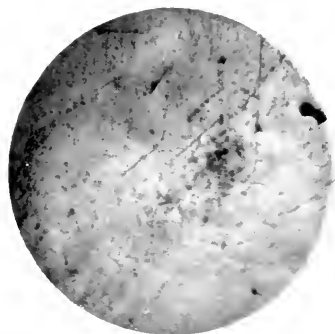


FIG. 13.—Steel: 0.16 per cent. Carbon.
Magnified 186 diameters.

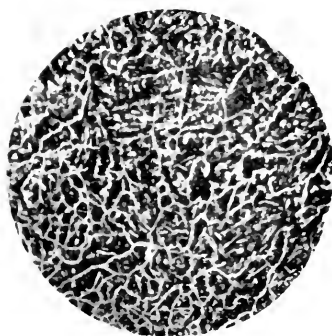


FIG. 14.—Steel: 0.29 per cent. Carbon.
Magnified 146 diameters.

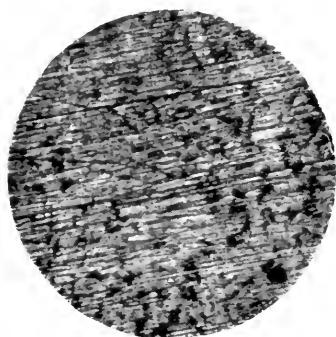


FIG. 15.—Steel: 0.33 per cent. Carbon.
Magnified 146 diameters.

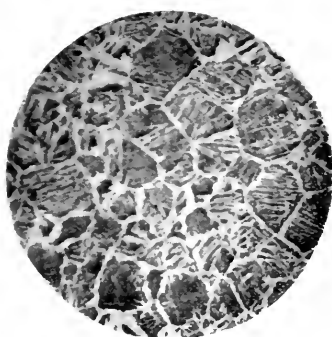


FIG. 16.—Steel: 1.16 per cent. Carbon.
Magnified 146 diameters.

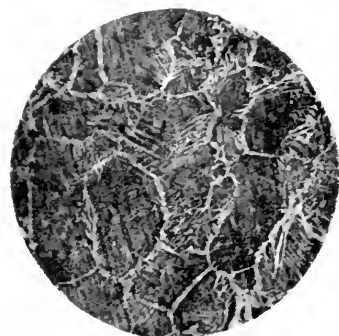


FIG. 17.—Steel: 1.04 per cent. Carbon.
Magnified 146 diameters.

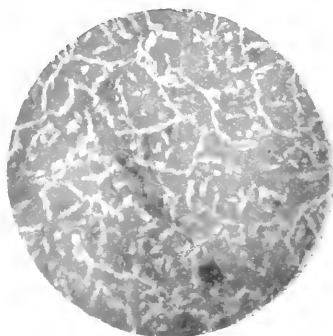


FIG. 18.—Steel: 0.48 per cent. Carbon.
Magnified 146 diameters.

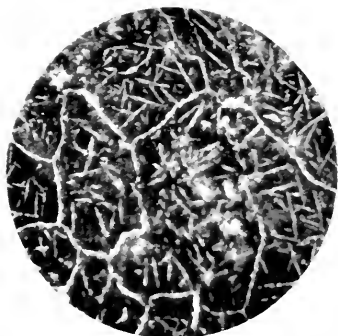


FIG. 19.—Steel: 1.57 per cent. Carbon.
Magnified 146 diameters.

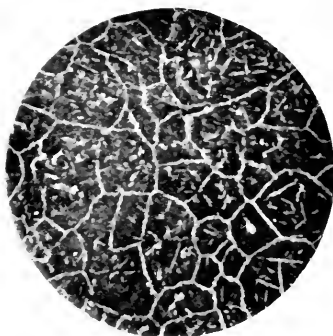


FIG. 20.—Steel: 1.19 per cent. Carbon.
Magnified 186 diameters.



FIG. 21.—Steel: 0.92 per cent. Carbon.
Magnified 186 diameters.

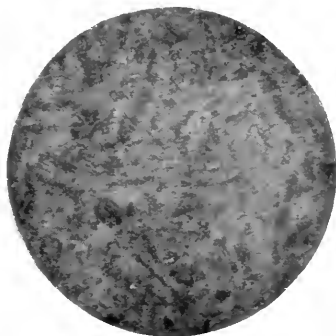


FIG. 22.—Steel: 0.44 per cent. Carbon.
Magnified 186 diameters.



FIG. 23.—Steel: 1.44 per cent. Carbon.
Magnified 186 diameters.



FIG. 24.—Steel: 1.51 per cent. Carbon.
Magnified 186 diameters.

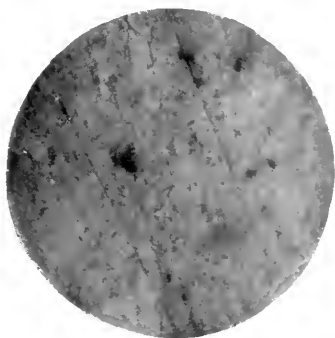


FIG. 25.—Steel: 0.39 per cent. Carbon.
Magnified 186 diameters.



FIG. 26.—Chromium Steel: 1.62 per cent. Carbon; 10.94 per cent. Chromium.
Magnified 186 diameters.

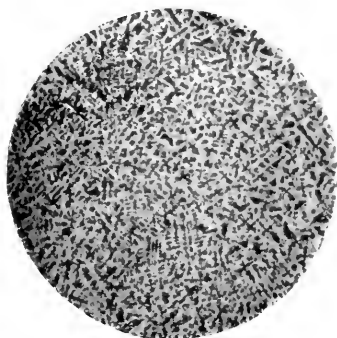


FIG. 27.—Chromium Steel: 1.56 per cent. Carbon; 8.83 per cent. Chromium.
Magnified 186 diameters.



FIG. 28.—Chromium Steel: 2.03 per cent. Carbon; 14.38 per cent. Chromium.
Magnified 146 diameters.



FIG. 29.—Chromium Steel: 1.74 per cent. Carbon; 8.00 per cent. Chromium.
Magnified 186 diameters.

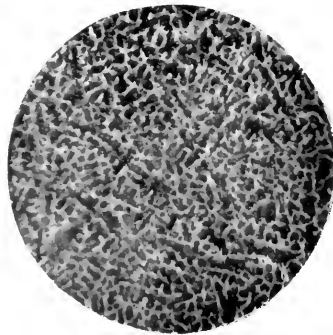


FIG. 30.—Chromium Steel: 1.99 per cent. Carbon; 5.52 per cent. Chromium.
Magnified 186 diameters.



PLATE XVIII



FIG. 31.—Molybdenum Steel: 0.30 per cent. Carbon; 3.52 per cent. Molybdenum. Magnified 186 diameters.



FIG. 32.—Molybdenum Steel: 0.50 per cent. Carbon; 5.38 per cent. Molybdenum. Magnified 186 diameters.

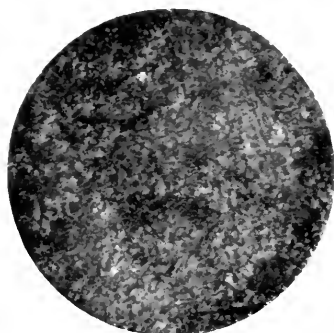


FIG. 33.—Molybdenum Steel: 0.46 per cent. Carbon; 2.62 per cent. Molybdenum. Magnified 186 diameters.

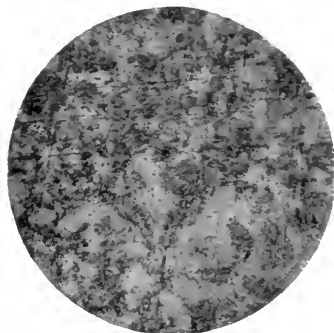


FIG. 34.—Tungsten Steel: 0.35 per cent. Carbon; 4.94 per cent. Tungsten. Magnified 186 diameters.

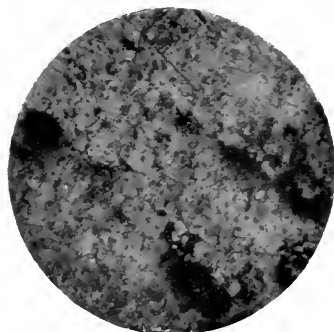


FIG. 35.—Tungsten Steel: 0.27 per cent. Carbon; 7.11 per cent. Tungsten. Magnified 186 diameters.



FIG. 36.—Tungsten Steel: 0.18 per cent. Carbon; 3.60 per cent. Tungsten. Magnified 186 diameters.



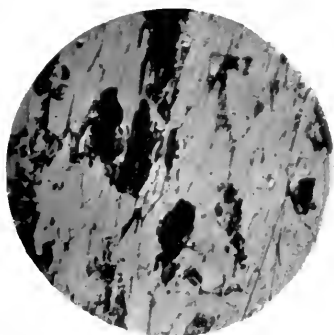


FIG. 37.—Ferro-chromium: 10.05 per cent. Carbon; 51.80 per cent. Chromium. Magnified 186 diameters.

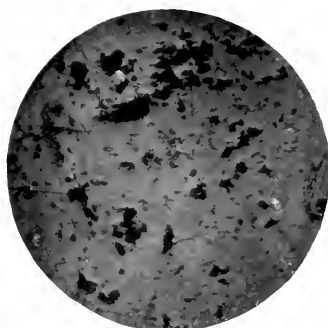


FIG. 38.—Ferro-chromium: 11.50 per cent. Carbon; 49.70 per cent. Chromium. Magnified 186 diameters.

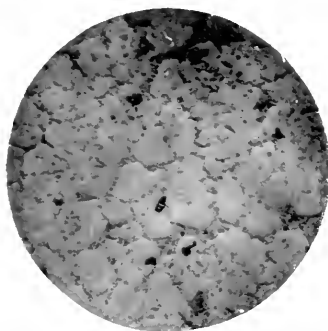


FIG. 39.—Ferro-chromium: 3.72 per cent. Carbon; 52.70 per cent. Chromium. Magnified 186 diameters.



FIG. 40.—Ferro-chromium: 6.50 per cent. Carbon; 50.60 per cent. Chromium. Magnified 186 diameters.



FIG. 41.—Ferro-chromium: 7.40 per cent. Carbon; 67.10 per cent. Chromium. Magnified 186 diameters.

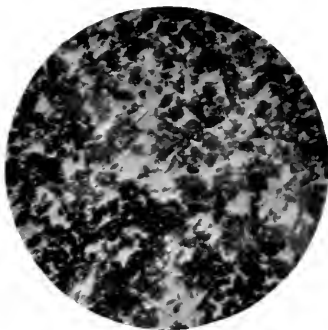


FIG. 42.—Ferro-molybdenum: 0.73 per cent. Carbon; 50.55 per cent. molybdenum. Magnified 186 diameters.

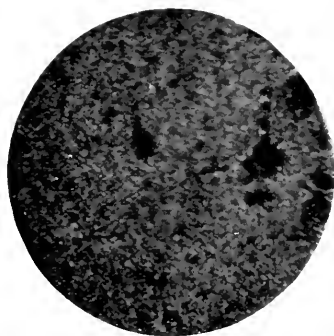


FIG. 43.—Ferro-tungsten: 1.77 per cent.
Carbon; 38.74 per cent. Tungsten.
Magnified 186 diameters.

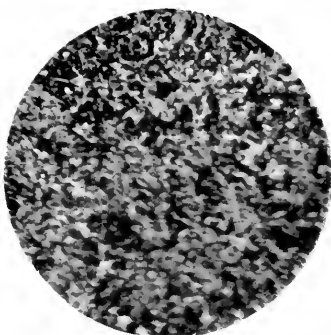


FIG. 44.—Ferro-tungsten: 1.82 per cent.
Carbon; 49.64 per cent. Tungsten.
Magnified 146 diameters.



FIG. 45.—Ferro-tungsten: 2.05 per cent.
Carbon; 41.39 per cent. Tungsten.
Magnified 146 diameters.

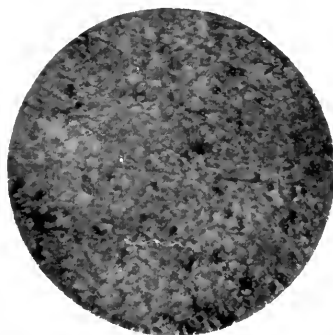


FIG. 46.—Ferro-tungsten: 2.51 per cent.
Carbon; 43.35 per cent. Tungsten.
Magnified 186 diameters.

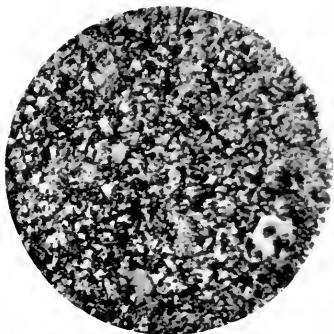
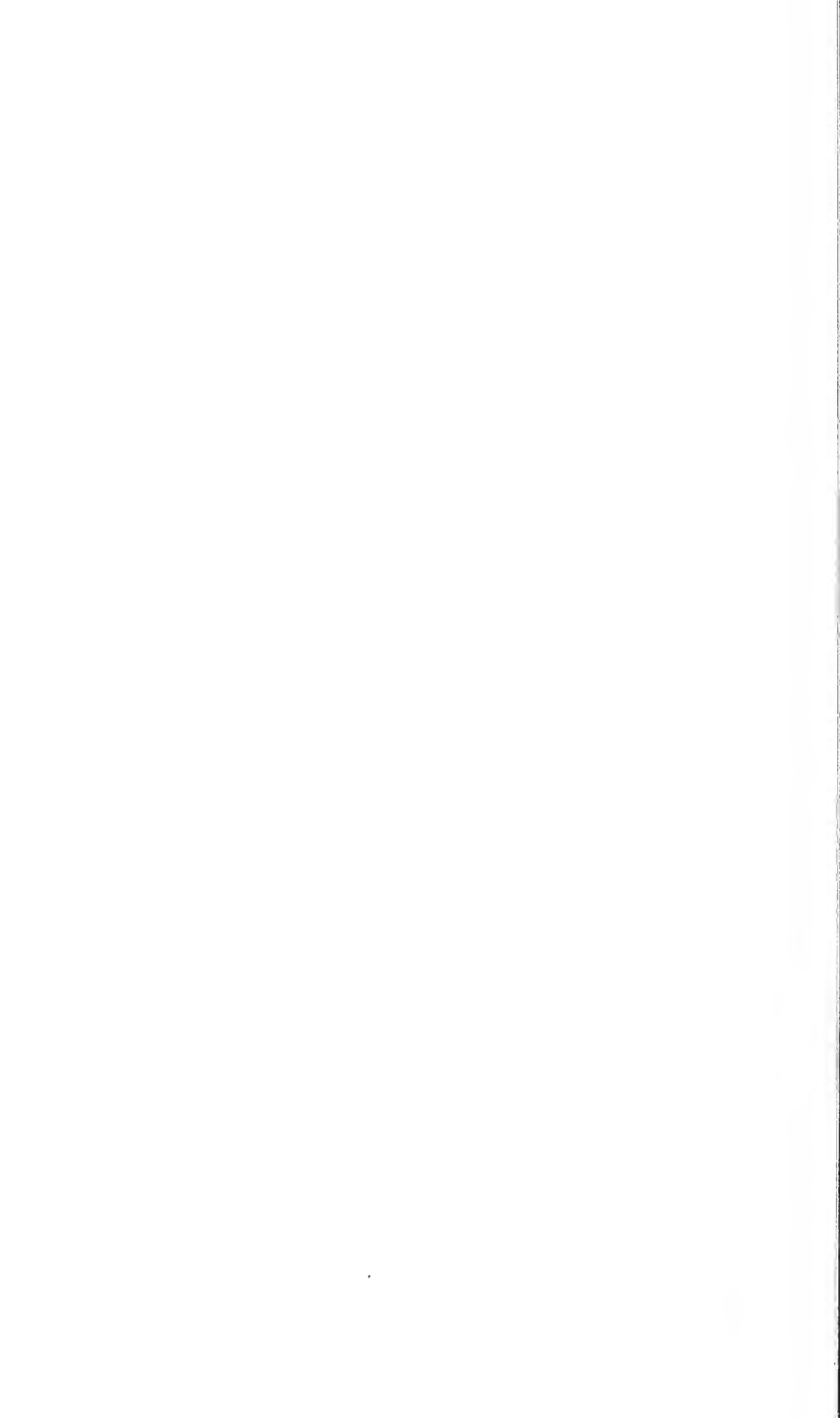


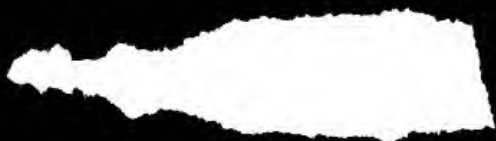
FIG. 47.—Ferro-tungsten: 2.04 per cent.
Carbon; 37.50 per cent. Tungsten.
Magnified 186 diameters.



FIG. 48.—Ferro-tungsten: 2.02 per cent.
Carbon; 59.01 per cent. Tungsten.
Magnified 146 diameters.







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